

PRINCIPLES AND APPLICATIONS  
OF  
ELECTROCHEMISTRY

*Volume I* Principles

BY H. JERMAIN CREIGHTON

*Volume II* Applications

BY W. A. KOEHLER

PRINCIPLES AND APPLICATIONS  
OF  
*Electrochemistry*

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IN TWO VOLUMES

*Volume I* — PRINCIPLES

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*Fourth Edition*

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## PREFACE TO THE FOURTH EDITION

The electrochemist may view with pleasurable and pardonable pride the rapid progress that has been made in his science during the present century, and may anticipate with confidence important developments in the future. On the theoretical side, notable advances have been made in our knowledge of the thermodynamic properties of solutions; of dielectrics; of irreversible processes, including electrolytic conductance and overvoltage; of the mechanism of the electrochemical oxidation and reduction of organic substances; and of the nature of proteins, to cite a few examples. Electrochemical industries which were young at the turn of the century have been expanded, and numerous others varying widely in nature have been developed. In consequence of this growth the curve for the consumption of electrochemical energy in this field shows a steep upward slope: between 1932 and 1936 this consumption increased nearly threefold and in the latter year amounted to twelve and a half billion kilowatt-hours. Today the electrochemical, electrothermal, and allied industries consume upward of 10 per cent of the electrical energy generated in this country and play an important part in the manufacture of products which affect the lives of all of us. Some of these electrochemical products can be produced by no other means; frequently the electrochemical method of formation is preferable, in point of both economy and superiority of product.

The purpose of this book, in its two volumes, is to present a systematic course of instruction in electrochemistry for chemistry students, and to provide a reference book for others interested in the subject. Its value in this respect is enhanced by the large amount of experimental data and numerous references to original papers throughout the text. Parts of the book are well suited for electrical engineers. The first volume deals with the principles and general theory of the subject; the second volume, by Professor W. A. Koehler, treats the more important technical applications of the science. The word "electrochemistry" in the title is employed in a broad sense and includes electrometallurgy and electrothermics.

In the present edition of *Principles of Electrochemistry* the entire text has been revised. This has afforded an opportunity of not only adding a number of new topics and deleting old material, but also of making many minor changes in the nineteen-year-old framework of the volume. The more important changes are as follows: (1) new sections have been introduced which deal with the structure and properties of the electric double layer, the study of electrophoresis by the moving-boundary

method, streaming potentials, polarographic analysis, the Wien effect, and glow discharge electrolysis; (2) the sections on fused electrolytes, the glass electrode, the applications of potentiometric measurements, the applications of electro-osmosis and electrophoresis, overvoltage, electrochemical reduction, and electrochemical action in gases have been extended; (3) several new figures and tables of data have been included. It is hoped that, thus revised, this volume will continue to meet with the cordial reception it has enjoyed during the past two decades.

As far as possible the author has employed the symbols recommended by the International Commission for the Unification of Physico-Chemical Symbols (cf. *Zeitschrift für Elektrochemie*, 27, 527, 1921). As regards the algebraic signs of potentials, the terminology adopted by the Electrochemical Society, the Bunsen Gesellschaft, and the National Bureau of Standards at Washington has been used.

In attempting to bring his *Principles of Electrochemistry* up to date in its several editions, the author has had the benefit of friendly and constructive criticisms from a number of teachers who have used it. He wishes here to express his warmest thanks to all of these, especially to Professor Grinnell Jones of Harvard University and to Professor John Warren Williams of the University of Wisconsin. The author is also indebted to Professor Colin G. Fink of Columbia University for reading and suggesting improvements in the original manuscript of this volume; to Professor Williams for much of the material from which the section on the polarity of molecules was prepared and for his criticism of this section; to Professor V. K. LaMer of Columbia University for permission to use portions of his paper dealing with the Debye and Hückel theory; to the Leeds and Northrup Company for their generosity in furnishing the cuts of several illustrations; and to his colleague, Dr. Walter B. Keighton, Jr., and to his son, Dr. R. H. J. Creighton, for suggestions and assistance in reading the proofs.

In concluding these prefatory remarks, it may not be inappropriate to state that the warm reception of the earlier editions of this volume is a source of deep satisfaction to its author; and the fact that it has filled a need, as shown by its continued demand, is more than ample compensation for the labor spent in its preparation and revisions.

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July, 1948

## SYMBOLS

The page numbers which accompany some of the symbols denote where they are used for the first time or where they are defined.

$A$	{ Empirical constant.
	{ Work or energy (page 172).
$\text{\AA}$	Ångström. $1\text{\AA} = 10^{-8}$ cm.
	{ Empirical constant.
$a$	{ Activity (page 303).
	{ Debye and Hückel's effective ionic diameter (page 322).
	{ Empirical constant.
$\alpha$	{ Degree of dissociation (page 37).
$B$	Empirical constant.
$b$	Empirical constant.
	{ Empirical constant.
$\beta$	{ The Debye and Hückel constant (page 320).
	{ Resistance of solution (page 69).
$C$	{ Effective ion concentration (page 184).
C.D.	Current density (page 24).
C.E.	Current efficiency (page 25).
	{ Concentration (usually molal or equivalent).
$c$	{ Conductance of solution (page 87).
	{ Velocity of light (page 5).
$D$	Empirical constant.
$d$	Density.
	{ Distance between two sides of an electric double layer (page 155).
$\delta$	{ Distribution coefficient (page 382).
	{ Hydrogen-ion concentration (page 418).
	{ Lowering of the freezing point (page 34).
$\Delta$	{ Temperature coefficient of ion conductance (page 135).
	{ Electromotive force, potential difference (page 2).
	{ Oxidation potential (page 230).
$E$	{ Overvoltage (page 247).
	{ Ionizing potential (page 441).
$E_o$	Normal oxidation potential (page 230).
E.E.	Energy efficiency (page 25).

$e$	{ Base of natural logarithms. Electrical charge (page 51). Unit electrical charge (page 316).
$\epsilon$	{ Epsilon potential (page 148). Dielectric constant (page 51).
$F$	The faraday = 96,494 coulombs (page 15).
$f$	{ Force. Mass-action function (page 297).
$f_o$	Osmotic coefficient (page 311).
$\phi$	Dilution, <i>i.e.</i> , the number of cubic centimeters of solution containing one mole or equivalent of electrolyte (page 68).
$\eta$	Coefficient of viscosity (page 96).
$\gamma$	Activity coefficient (page 305).
$h$	{ Height. Quantum constant (page 441).
$I$	Current strength (page 2).
$i$	Mole number (page 35).
$J$	Electrical (or mechanical) equivalent of heat (page 9).
$K$	{ Cell constant (page 85). Mass-action constant (page 185). Dissociation constant (page 290). Indicator function (page 401).
$K_a$	Acidic dissociation constant (page 410).
$K_b$	Basic dissociation constant (page 410).
$K_i$	Indicator constant (page 400).
$K_0$	Apparent dissociation constant of ampholytes (page 416).
$k$	{ Empirical constant. Boltzmann's constant (page 57). Reaction velocity constant (page 289).
$k_a$	{ Dissociation constants of amino acids (page 421).
$k_b$	
$\kappa$	{ Specific conductance (page 67). Debye and Hückel's reciprocal distance (page 317).
$L$	Solubility product (page 424).
$l$	Distance or length.
$l_a$	{ Ion conductance (page 134).
$l_c$	
$\Lambda$	Equivalent conductance (page 68).
$\lambda$	Wavelength (page 441).
$M$	{ Molecular weight. Mass.
$m$	Mass.

$\mu$	{ Electric moment (page 56). Molal conductance (page 68). Ionic strength (page 308).
<b>N</b>	Avogadro's number (page 39).
<i>N</i>	Mole fraction (page 33).
<i>n</i>	{ Number. Number of ions, molecules or moles. Refractive index (page 58).
<i>n<sub>a</sub></i>	Transference number of anion (page 116).
<i>n<sub>c</sub></i>	Transference number of cation (page 116).
$\nu$	Number of ions in a molecule (page 37).
<i>P</i>	{ Pressure. Osmotic pressure (page 33). Molar polarization (page 56).
<b>P</b>	Electrolytic solution pressure (page 175).
<i>p</i>	Gas or vapor pressure (page 33).
<i>pH</i>	Reciprocal of logarithm of hydrogen-ion concentration (page 217).
<b>II</b>	Volta effect (page 183).
$\pi$	{ Number = 3.14159. Electrode potential (page 181). Liquid-junction potential (page 202).
$\pi_c$	Electrode potential, referred to the normal calomel electrode (page 192).
$\pi_h$	Electrode potential, referred to the normal hydrogen electrode (page 192).
$\pi^\circ$	Electrolytic potential (page 193).
<i>Q</i>	{ Quantity of electricity (page 7). Quantity of heat.
<i>q</i>	{ Quantity of heat. Heat of reaction (page 172). Cross-section.
<i>R</i>	{ Resistance (page 2). The gas constant (page 33).
<i>r</i>	Radius.
$\rho$	{ Molal heat of fusion (page 34). Average density of electricity (page 315). Solubility (page 323).
<i>S</i>	{ Sum of concentrations of undissociated forms of an ampholyte (page 412).
$\sigma$	Function in the Debye and Hückel theory (page 321).
$\sum$	Summation.
<i>T</i>	Absolute temperature.



## CHAPTER I

### INTRODUCTION

Electrochemistry, that division of chemistry which deals with the relations between, and the mutual transformations of, chemical and electrical energy, owes its birth to the discoveries of Volta which culminated in the invention of the voltaic pile towards the end of the eighteenth century. This important tool was almost immediately employed by Sir Humphry Davy to study the chemical action of electric currents and to isolate potassium and sodium from the molten hydroxides of these elements, memorable pioneer work which paved the way towards the development of a modern electrochemical industry of large proportions. But Davy's most significant service to science was his finding and training Michael Faraday, to whom more than anyone else electrochemistry is indebted. To this experimental genius are due not only the discovery and enunciation of the two laws upon which so much of electrochemistry is practically based, but also the principle of electromagnetic induction which led ultimately to an economical means of generating energy, essential for the industrial application of electrochemistry. As a result of these brilliant achievements and the valuable contributions of Kolbe, Hittorf, Clausius, Arrhenius, Nernst, Castner, Haber, Hall, and others, the nineteenth century will always be outstanding for its great discoveries in electrochemistry and its astonishing developments in the industrial application of this science, not to mention the rich heritage it provided for electrochemists of the twentieth century.

**Electric Currents and Their Properties.** A Daniell cell (Fig. 1) consists of metallic zinc immersed in a solution of zinc sulphate and metallic copper immersed in a solution of copper sulphate, the zinc being charged negatively and the copper positively. On joining the two metals, or poles, of this cell by a wire, the temperature of the wire rises. If the wire is cut and there are attached to the two ends small squares of platinum foil which are then immersed in a solution of copper sulphate, red metallic copper is deposited on one of the pieces of foil. These phenomena indicate that *something takes place in the wire joining the poles of a Daniell cell—a current of electricity is said to flow through the*

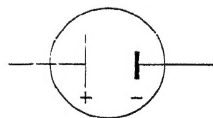


Fig. 1.



wire. Since a magnetic needle placed above the wire connecting the poles of a Daniell cell is always deflected in the same direction, and since copper is always deposited on the piece of platinum foil connected to the zinc pole, we may infer that the current *flows in a definite direction*. The **direction of the current** has been arbitrarily defined as the direction in which the positive current would have to flow in order to produce observed magnetic effects. It has been found that the weight of copper deposited upon the platinum foil in a given time is *less*, when the length of the wire joining the poles of the Daniell cell is *increased*. It would appear, therefore, that the resistance to the flow of the electric current through the wire is augmented by increasing its length. Experiment has shown that the weight of copper deposited on the platinum foil and,

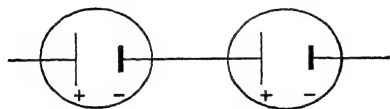


FIG. 2.

therefore, the **current strength** ( $I$ ) vary inversely as the length, or the **resistance** ( $R$ ), of the wire. When two Daniell cells are connected in series (Fig. 2) by joining the zinc pole of one to the copper pole of the

other, then, on attaching a piece of platinum foil to the other pole of each cell and immersing them in a solution of copper sulphate, it is found that the weight of copper deposited on the foil, in a given time, is twice as great as when only one cell is employed, i.e., *a greater current of electricity flows through the wire*. In some way, this combination of the two cells increases the electrical pressure or force—**electromotive force** ( $E$ )—which drives the electric current through the **circuit**. The current strength varies directly as this electrical pressure or electromotive force.

The relation between the three fundamental quantities, current strength, resistance, and electromotive force, is expressed by **Ohm's law**, which states: *the current strength is directly proportional to the electromotive force and inversely proportional to the resistance, i.e.,*

$$I = \frac{E}{R} \quad (1)$$

A clearer conception of resistance and electromotive force may be gained by comparing the flow of electricity through a wire with the passage of water through a pipe. When water from a large reservoir,  $A$ , Fig. 3, flows through a narrow, horizontal, uniform tube,  $CD$ , on which is placed a number of vertical manometer tubes,  $B$ , the height of water in these tubes, which is a measure of the hydrostatic pressure at the point where the manometer tube joins the horizontal tube, varies directly as the distance of the vertical tube from the reservoir. This variation in pressure is shown diagrammatically in Fig. 4. The pressure

at the entrance to the horizontal tube is represented by the perpendicular  $CC'$ , and the pressures at different points in the horizontal tube by the

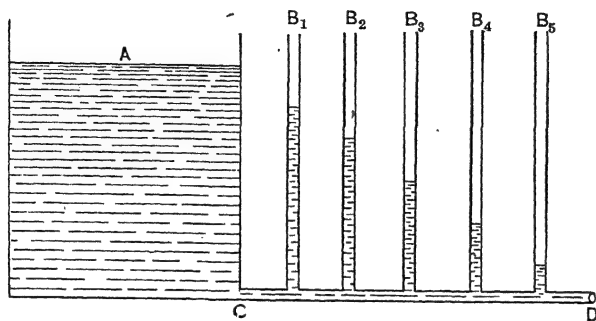


FIG. 3.

corresponding perpendiculars to the right. The difference in pressure between two points,  $B_1$  and  $B_2$ , on the horizontal tube is represented by  $b_1B'_1$ . This difference is greater, the more widely the two points are separated. The same considerations may be extended to the flow of electricity through a wire. Suppose that the two terminals,  $A$  and  $B$  (Fig. 5), of some source of electromotive force (e.g., a Daniell cell or a dynamo) are joined by a uniform wire, of small diameter, 100 meters in length. Just as in the water pipe, there is a uniform drop in the electrical pressure, or a potential fall, along the wire between  $A$  and  $B$ . Between any two points,  $D$  and  $D'$ , on the wire there exists a

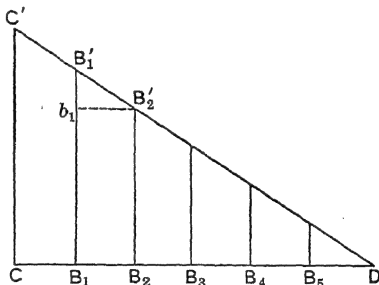


FIG. 4.

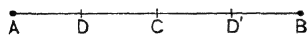


FIG. 5.

**potential difference** (p.d.), which is greater the more widely the points are separated. The potential difference between  $A$  and the middle point,  $C$ , of the wire is equal to that between  $C$  and  $B$ . The closer the points  $D$  and  $D'$  approach to  $A$  and  $B$ , respectively, the more nearly the potential difference between  $D$  and  $D'$  approaches the electromotive force of the source (i.e., that of the terminals  $A$  and  $B$ ). The sum of the potential differences in the different parts of the wire (e.g., the potential differences between  $AD$ ,  $DC$ ,  $CD'$ , and  $D'B$ , in Fig. 5) is equal to the electromotive force of the source.

In a circuit made up of a Daniell cell and a wire joining the copper and zinc poles, the current flows not only through the wire, but also through the solution in the cell. The total resistance of the circuit is made up of the resistance of the wire—the external resistance,  $R_{ex.}$ —and the resistance of the solution—the internal resistance,  $R_{in.}$  The electromotive force,  $E$ , of the cell is equal to the sum of the fall of potential,  $E_{in.}$ , in the internal resistance and that,  $E_{ex.}$ , in the external resistance. Since the fall of potential in any part of the circuit is directly proportional to the resistance of that part, it follows that

$$\frac{E}{E_{ex.}} = \frac{E_{ex.} + E_{in.}}{E_{ex.}} = \frac{R_{ex.} + R_{in.}}{R_{ex.}}$$

and

$$\frac{E}{E_{in.}} = \frac{E_{ex.} + E_{in.}}{E_{in.}} = \frac{R_{ex.} + R_{in.}}{R_{in.}}$$

whence

$$E_{ex.} = E \frac{R_{ex.}}{R_{ex.} + R_{in.}} \quad (2)$$

and

$$E_{in.} = E \frac{R_{in.}}{R_{ex.} + R_{in.}} \quad (2a)$$

From equation 2 it is evident that, the greater the external resistance, the more nearly the fall of potential in the external circuit approaches the electromotive force of the cell. Only when the external resistance is infinitely great, as when the external circuit is broken, or when the internal resistance is zero, is the fall of potential in the external circuit equal to the electromotive force of the cell. It is for this reason that the resistance of voltmeters is usually very large.

When the wires from the poles of a Daniell cell are touched to a piece of moist potassium iodide-starch paper, a dark blue spot always appears on the paper under the wire joined to the copper, or positive, pole of the cell. This behavior affords a convenient means of *determining the polarity* of the terminals of a source of electricity.

It has been mentioned that the current from a Daniell cell always flows in one direction. Though it is customary to regard the current as flowing through the external resistance from the negative pole to the positive, the opposite view could be taken. A current which flows in one direction is called a continuous or **direct current**. Voltaic or galvanic cells, like the Daniell cell, always produce direct currents. There exist, however, sources of electricity from which the current flows first in one

and then in the opposite direction. Such a current is called an **alternating current**. The number of times the direction of flow of this kind of current is changed per second is termed the **frequency** of the current.

**Electrical Units.** Two different systems of *absolute cgs* units are employed for measuring electrical quantities, both of which are derived from the fundamental units of length, mass, and time. These are the *electrostatic* system of units (esu) which are derived from the effects of electrostatic attraction and repulsion, and the *electromagnetic* system of units (emu) which are derived from the effects of the repulsion between two like magnetic poles.<sup>1</sup> The ratio of an electromagnetic to the corresponding electrostatic unit is an exact multiple or submultiple of a constant ( $c$ ), the value of which is  $3.00 \times 10^{10}$ . Incidentally, it may be mentioned that, within the limits of experimental error, this value is identical with the velocity of light. This remarkable relation is of important theoretical significance and gives, as Maxwell showed, the velocity of propagation of electromagnetic waves, this velocity being exactly equal to the velocity of light.

Since many of the cgs units in both the electromagnetic and the electrostatic systems are inconveniently large or small for the expression of the electrical quantities in ordinary work with electricity, a system of *practical* units which is almost exclusively employed in electrical science, electrochemistry, and electrical engineering has been formulated. In this system the units of all electrical quantities are exact decimal multiples or submultiples of the corresponding electromagnetic units. In order to facilitate the expression of electrical quantities in terms of these units, a number of governments and different congresses of electrical engineers have adopted substantial equivalents of certain units which are more easily realized experimentally. These substantial equivalents are designated *international units* for the purpose of distinguishing them from the true (practical) units.

The practical unit of current strength is called an **ampere**, in honor of the French physicist and chemist, A. M. Ampère (1775–1836). One ampere is one-tenth of the electromagnetic unit of current strength, the electromagnetic unit being defined as the strength of a current which, when flowing through a wire in the form of an arc 1 centimeter in length and 1 centimeter in radius, exerts a force of 1 dyne on a unit magnet pole placed at the center. The international ampere is defined as the current strength which deposits 1.11800 milligrams of silver or 0.3294 milligram of copper from suitable solutions of salts of these metals in one

<sup>1</sup> The derivation, definition, and dimensions of these units will be found in textbooks on physics.

second. Current strength may be measured by means of an instrument called an **ammeter**.

The practical unit of electrical resistance is called an **ohm**, after the German physicist, G. S. Ohm (1787-1854), who discovered the relation between  $I$ ,  $E$ , and  $R$  which bears his name. One ohm is equal to  $10^9$  electromagnetic units of resistance, 1 electromagnetic unit being the resistance of a wire, or **conductor**, when unit potential difference between its ends produces a current strength of 1 electromagnetic unit. The international ohm is equal to the resistance of 14.4521 grams of mercury in the form of a column of *uniform* cross section and 106.3 centimeters in length, at  $0^\circ$  C. Some substances have a lower resistance than mercury, others a higher resistance. Table I shows the resistances of a number of substances relative to that of mercury at  $0^\circ$  as unity.

TABLE I  
RELATIVE RESISTANCES  
(Mercury = 1)

Substance	Resistance	Substance	Resistance
Silver	0.015	Platinum	0.137
Copper	0.0167	Lead	0.20
Gold	0.02	German silver	0.3-0.5
Aluminum	0.03	Manganin	0.48
Zinc	0.06	Nichrome	ca. 1
Nickel	0.07	Compressed $\text{PbO}_2$	2.3
Brass	0.07-0.09	Graphite	11-14
Iron	0.09-0.15	Arc carbon	39-55

The practical unit of electromotive force (and of potential difference) is called a **volt**, in recognition of the work of the Italian physicist, Count A. Volta (1745-1827). One volt is equal to  $10^8$  electromagnetic units of electromotive force, 1 electromagnetic unit being the potential difference which exists between two points when the expenditure of 1 erg of work is required to bring a unit of positive electricity from one point to the other against the electric force. The international volt is the electromotive force required to maintain a current of 1 ampere through a conductor having a resistance of 1 ohm; or it is equal to  $\frac{100,000}{101,827}$  of the electromotive force of the Weston standard cell at  $20^\circ$  (see page 169). A **voltmeter** is an instrument for measuring electromotive force and potential difference.

Just as the quantity of water which passes through a pipe is determined by the strength of the current and the time during which the water is

flowing, so the quantity of electricity ( $Q$ ) which flows through a conductor depends on these same factors. The unit quantity of electricity is called a **coulomb** in honor of the French physicist, C. A. Coulomb (1736-1806). One coulomb is one-tenth of the electromagnetic unit of quantity, the electromagnetic unit being the quantity of electricity conveyed through the cross section of a conductor by 1 electromagnetic unit of current in unit time. Thus, whether 4 amperes flow through a conductor for  $\frac{1}{2}$  second, or 1 ampere for 2 seconds, the quantity of electricity which passes through a cross section is, in each case,

$$Q = I \times t = 2 \text{ coulombs}$$

Quantity of electricity is measured by means of an instrument called a **coulometer** (see Chapter II). Since an ampere (international) is that current strength which deposits 1.11800 milligrams of silver from a solution of a silver salt in 1 second, the number of coulombs of electricity which passes through the solution may be obtained by dividing the weight (expressed in milligrams) of silver deposited by 1.11800. By placing a silver coulometer in series in an electric circuit, the quantity of electricity which passes through the circuit can be calculated as indicated.

Energy, which may be defined as that which produces changes in the properties of bodies, manifests itself in different forms: kinetic energy, thermal energy (heat), gravitational energy, cohesion energy, chemical energy, electrical energy, etc. The unit of electrical energy is called a **volt-coulomb** or a **joule**, after the English experimenter, J. P. Joule (1818-1889). Like other forms of energy, electrical energy can be resolved into an intensity factor and a capacity factor. For electrical energy, these factors are electromotive force and quantity of electricity, respectively. Thus,

$$\begin{aligned} \text{Electrical energy} &= \text{Emf} \times \text{Quantity of electricity} \\ &= \text{Volts} \times \text{Coulombs} \\ &= \text{Joules} \end{aligned}$$

Accordingly, whether a current strength of 2 amperes is maintained by an electromotive force of  $\frac{1}{2}$  volt, or a current strength of 1 ampere is maintained by an electromotive force of 1 volt, the quantity of electrical energy developed is 1 joule per second.

Since power represents the amount of energy developed per second, it follows that the unit of electrical power is that power which will develop

1 joule of electrical energy per second. To this unit the name **watt** has been given, in honor of James Watt (1736-1819), the Scotch inventor.

$$1 \text{ watt} = 1 \text{ joule per second}$$

$$746 \text{ watts} = 1 \text{ horsepower (hp)}$$

$$\text{Elec. power} = \frac{\text{Joules}}{\text{Seconds}} = \frac{\text{Volt-coulombs}}{\text{Seconds}} = \text{Volt-amperes} = \text{Watts}$$

Hence

$$1 \text{ watt-second} = 1 \text{ joule}$$

Since the watt-second or joule is very small, larger units, such as the

$$\text{Watt-hour} = 3600 \text{ joules}$$

$$\text{Kilowatt-hour (kw-hr)} = 3,600,000 \text{ joules}$$

$$\text{Kilowatt-year (kw-yr)} = 31,536 \times 10^6 \text{ joules}$$

are very frequently employed for expressing quantities of electrical energy.

TABLE II  
ELECTRICAL UNITS

Unit	Relations			
	Practical Unit			$\frac{\text{Emu}}{\text{Esu}}$
	Name	Equivalent in Absolute Units in the Cgs System		
		Emu	Esu	
Resistance	Ohm	$10^9$	$\frac{1}{9} \times 10^{-11}$	$c^2$
Current strength	Ampere	$10^{-1}$	$3 \times 10^9$	$1/c$
Potential or electromotive force	Volt	$10^8$	$1/300$	$c$
Quantity	Coulomb	$10^{-1}$	$3 \times 10^9$	$1/c$
Capacitance	Farad	$10^{-9}$	$9 \times 10^{11}$	$1/c^2$
Inductance	Henry	$10^9$	$\frac{1}{9} \times 10^{-11}$	$c^2$
Energy	Joule	$10^7$ ergs		
Power	Watt	$10^7$ ergs per second		

The practical unit of **capacitance** is called a **farad**, after the celebrated English chemist, Michael Faraday (1791–1867). One farad is the capacitance of a condenser such that a potential difference of 1 volt across its terminals gives it a charge of 1 coulomb. A farad is equal to  $10^{-9}$  electromagnetic unit of capacitance, one of which requires unit quantity to charge it to unit potential.

The practical unit of **inductance** is called a **henry**, named in honor of the great American physicist, Joseph Henry (1799–1878). One henry is the inductance in a circuit when the induced emf in this circuit is 1 volt, while the inducing current varies at the rate of 1 ampere per second. One henry is equal to  $10^9$  electromagnetic units of inductance, the electromagnetic unit being such that unit emf is induced by the variation of the current at the rate of 1 unit per second.

The relations between electromagnetic, electrostatic, and practical units are summarized in Table II.

**The Relation between Electrical and Thermal Energies.** All forms of energy can be converted into heat, in accordance with the first law of thermodynamics, which states: "When a quantity of energy disappears at any place, a precisely equal quantity of energy simultaneously appears at some other place or places, and when a quantity of energy disappears in any form, a precisely equal quantity of energy appears in some other form or forms; equal quantities of different forms of energy being understood to be such quantities as produce the same effect when converted into the same form."<sup>1</sup> Thus, it has been found that 0.4272 kilogram-meter of mechanical energy can be converted into an amount of heat sufficient to raise the temperature of 1 gram of water from 17° to 18°; that is, this quantity of mechanical energy is equivalent to 1 calorie of heat. The number 0.4272 is the factor by which heat units (calories) must be multiplied in order to convert them into mechanical units (kilogram-meters). This factor is called the **mechanical equivalent of heat**.

When an electric current is allowed to flow through a circuit in such a way that no work is performed, the entire electrical energy developed is converted into thermal energy. The quantity of heat so produced can be determined by enclosing the circuit in a calorimeter. Experiment has shown that 4.182 joules of electrical energy are invariably required to produce 1 calorie of heat. The **electrical equivalent of heat** (i.e., the factor by which heat units must be multiplied to convert them into units of electrical energy) is, therefore, **4.182 = J**. Conversely,

$$1 \text{ joule} = 0.2387 \text{ calorie} = 10^7 \text{ ergs}$$

<sup>1</sup> Noyes, *General Principles of Physical Science*, p. 76, 1902.



If a current strength of 10 amperes, maintained by a constant electromotive force of 100 volts, is available, the electrical energy developed in 5 minutes is equivalent to

$$\frac{10 \times 100 \times 5 \times 60}{4.182} = 71,737 \text{ calories}$$

The amount of heat evolved when a quantity of electrical energy is converted into thermal energy may be calculated in another way. Let  $Q$  coulombs represent a quantity of electricity which is forced through a wire by an electromotive force of  $E$  volts. Then, the electrical energy available is  $EQ$  joules. If this electrical energy is converted into thermal energy, we have

$$\frac{EQ}{J} = q \text{ calories}$$

On dividing both sides of this equation by the number of seconds,  $t$ , during which the current flows through the circuit, we get

$$\frac{E(Q/t)}{J} = \frac{q}{t}$$

Since  $Q/t = I$  amperes, it follows that

$$\frac{EI}{J} = q'$$

where  $q'$  is the quantity of heat developed in 1 second. On combining this equation with Ohm's law, we obtain

$$\frac{I^2 R}{J} = q' \quad (3)$$

Thus, if a current of 5 amperes is maintained through a resistance of 8 ohms, the electrical energy developed in 1 second is equivalent to

$$\frac{(5^2) \times 8}{4.182} = 47.8 \text{ calories}$$

The heat produced by the union of 12 grams of carbon with 32 grams of oxygen is sufficient to raise the resulting 44 grams of carbon dioxide to a temperature of 4200°. Owing to losses of heat by radiation, to incomplete combustion, to dissociation of the carbon dioxide, and to the use of air instead of oxygen, the highest temperatures reached in practice by the combustion of fuel seldom exceed 1800°. On the other hand, the

highest temperature attainable by the conversion of electrical energy into thermal energy is limited only by radiation losses and the volatility of the electrodes and the resistor. Although otherwise the temperature could be raised indefinitely by simply increasing the current strength, as is evident from equation 3, the maximum temperature available by electrical heating is about  $3500^{\circ}$ . The practical attainment of very high temperatures by electrical heating has led to the development of a number of important so-called **electrothermic processes**, such, for example, as the production of calcium carbide, Carborundum, Alundum, and graphite. Though, strictly speaking, these are not electrochemical processes,<sup>1</sup> in that electrical energy, *per se*, is not directly transformed into chemical energy, they are usually treated as such and, accordingly, will be considered in Vol. II.

### PROBLEMS

1. The poles of a Daniell cell ( $E = 1.10$  volts), with an internal resistance of 10 ohms, are connected by a wire having a resistance of 100 ohms. This resistance is enclosed in a calorimeter. Calculate the quantity of heat developed in 20 hours.

2. A current is maintained in a wire having a resistance of 100 ohms by an electromotive force of 220 volts. All the electrical energy developed is converted into heat. What is the power used, and how many calories are produced per hour?

3. Suppose an electric current of 2.5 amperes to be available. Calculate the resistance required to generate enough heat to raise 500 grams of water from  $17^{\circ}$  to  $100^{\circ}$  in 30 minutes. (In solving this problem, it may be assumed that the specific heat of water is unity between the above temperatures, and that no heat is lost by radiation.)

4. The heat developed by maintaining a current of 4.3 amperes through a resistance of 30 ohms, placed in a thermostat of 500-liter capacity, is sufficient to keep the water at a constant temperature of  $25^{\circ}$ . How many degrees will the temperature of the thermostat fall in 40 minutes after the current is switched off?

5. A thermostat having a capacity of 1000 liters is to be kept at a constant temperature of  $25^{\circ}$  by the heat developed by passing an electric current through a resistance placed in the thermostat. Calculate the resistance it will be necessary to employ, when an electromotive force of 110 volts is available, and when the loss of heat by radiation is 200,000 calories per hour.

6. Assuming that the heat losses from the sides and top of an aluminum reduction furnace are 500,000 calories per square foot per hour, and its external dimensions are 5 feet by 7 feet by 2 feet, calculate the energy input required to balance the heat loss.

<sup>1</sup> Berthelot (*Compt. rend.*, 144, 53 [1907]) has pointed out that chemical reactions which occur at high temperatures, developed in a reaction mixture electrically, may be entirely different from those which take place when the heat is produced by fuel.

## CHAPTER II

### FARADAY'S LAWS OF ELECTROLYSIS

**Conductors.** In the main, conductors of electricity may be sharply divided into two classes: (1) **metallic or electronic conductors**, and (2) **electrolytic conductors**. The metals, alloys, and a few other substances, such as carbon, are conductors of the first class; certain salt solutions, molten salts, and a few solids, such as the halides of silver <sup>1</sup> and the  $\alpha$ -form of silver sulphide <sup>2</sup> (stable above 179°), constitute conductors of the second class. The passage of electricity through an electrolytic conductor is known as **electrolysis**. The dissolved or molten salt is termed an **electrolyte**. In metallic conductors, the passage of electricity takes place without the movement of any ponderable quantity of matter; in conductors of the second class, the passage of the current is invariably associated with the transport of matter. Besides this, there is another important difference between the two classes of conductors: with the exception of amorphous carbon, the resistance of conductors of the first class increases with rise in temperature; that of conductors of the second class decreases with increase in temperature. The change of resistance of conductors with temperature is expressed by the equation

$$R_t = R_{t_0} \left[ 1 + \frac{dR}{dt} (t - t_0) \right] \quad (1)$$

where the temperature coefficient of resistance,  $dR/dt$ , is positive for metals and alloys, and negative for amorphous carbon, graphite, and conductors of the second class.

A few substances have been investigated which appear to bridge the gap between the first and second classes of conductors. Conduction in these substances is part metallic and part electrolytic; therefore these substances have been called **mixed conductors**. For example, the  $\beta$ -form of silver sulphide (stable below 179°) is a mixed conductor, about 80 per cent of the conduction being electrolytic and the remaining 20 per cent

<sup>1</sup> Tubandt, *Z. anorg. Chem.*, **115**, 105 (1921).

<sup>2</sup> Tubandt, Eggert, and Schibbe, *ibid.*, **117**, 1 (1921).

metallic.<sup>1</sup> At temperatures above 200°, many metallic salts, especially halides, have been found to act as electrolytic conductors.<sup>2</sup> The electrolysis of solid solutions of oxygen in zirconium has been studied between 1600° and 1800°, and it has been found<sup>3</sup> that the oxygen moves through the lattice, thus increasing its concentration at the positive end of the conductor. According to the investigations of Kraus,<sup>4</sup> conduction in solutions of the alkali and alkaline-earth metals in liquid ammonia is part metallic and part electrolytic.

As we have already seen, there is a movement of matter when a current from a Daniell cell is passed through a solution of copper sulphate—copper is deposited on the piece of platinum foil joined to the zinc pole of the cell. A solution of copper sulphate is, therefore, an electrolytic conductor. Aqueous solutions of acids, bases, most inorganic salts, and many organic compounds are likewise conductors of this kind. Solutions in organic and other inorganic solvents are also capable of conducting the electric current, although their capacity for conduction is usually markedly less than that of aqueous solutions. Some non-aqueous solutions, however, have a high capacity for conduction. For example, solutions of certain salts in pure hydrocyanic acid are excellent conductors,<sup>5</sup> and a solution of sodium ethyl in zinc ethyl conducts an electric current as well as a 0.1 normal aqueous solution of potassium chloride.<sup>6</sup>

**The Products of Electrolysis.** When pieces of platinum foil, attached to the two poles of a Daniell cell, are immersed in an aqueous solution<sup>7</sup> of copper chloride, not only is copper deposited on the piece of foil joined to the negative pole of the cell, but also bubbles of chlorine are liberated at the other piece of foil. These pieces of foil are called **electrodes**. The electrode attached to the positive pole of the cell is termed the **anode**; that joined to the negative pole, the **cathode**.

During the passage of an electric current through an electrolytic conductor, the constituents of the electrolyte move through the solution

<sup>1</sup> Tubandt, Eggert, and Schibbe, *loc. cit.* The electrical properties of silver sulphide have been discussed by Vinal, *Bur. Standards, Sci. Paper*, No. 310 (1917). The mechanism of mixed conductors is discussed by Šmekal, *Z. physik. Chem.*, **5B**, 60 (1929); see also *Chem. Soc. Ann. Repts.*, **1937**, 154-7.

<sup>2</sup> Schmidt, *Z. Elektrochem.*, **30**, 440 (1924).

<sup>3</sup> Boer and Fast, *Rec. trav. chim.*, **59**, 161 (1940).

<sup>4</sup> *J. Am. Chem. Soc.*, **30**, 1323 (1908); **36**, 864 (1914); *Trans. Am. Electrochem. Soc.*, **45**, 412 (1924).

<sup>5</sup> Cf. Pearce, *J. Phys. Chem.*, **19**, 14 (1915).

<sup>6</sup> Cf. Hein, *Z. Elektrochem.*, **28**, 469 (1922).

<sup>7</sup> Hereafter, unless otherwise stated, by "solution" will be meant an aqueous solution.

and are liberated at the electrodes, as in the electrolysis of copper chloride. This, however, is not always evident, owing to the fact that the substances set free at the electrodes sometimes react with the solvent of the solution. The products of these reactions may be observed at the electrodes. The products of many electrolytes, such as the alkali metal salts of oxygen acids, and the alkali hydroxides, are simply hydrogen at the cathode and oxygen at the anode. Formerly, it had been supposed that the formation of these gases was a secondary process, due to the interaction with water of the metal and acid radical which were set free by the current. It is now known, however, that the electrolysis of such solutions consists in a *primary* decomposition of water, except under very special conditions (see page 264).<sup>1</sup> During the electrolysis of such solutions, concentration changes occur near the electrodes; the solution about the cathode becomes alkaline, and that about the anode, acid. Table III lists the products of electrolysis of solutions of a number of

TABLE III  
PRODUCTS OF ELECTROLYSIS

Electrolyte	Cathode Product	Anode Product
HCl (concd.)	H <sub>2</sub>	Cl <sub>2</sub>
H <sub>2</sub> SO <sub>4</sub>	H <sub>2</sub>	O <sub>2</sub>
NaOH, KOH	H <sub>2</sub>	O <sub>2</sub>
NaNO <sub>3</sub>	H <sub>2</sub> and NaOH	O <sub>2</sub> and HNO <sub>3</sub>
K <sub>2</sub> SO <sub>4</sub>	H <sub>2</sub> and KOH	O <sub>2</sub> and H <sub>2</sub> SO <sub>4</sub>
CuSO <sub>4</sub>	Cu	O <sub>2</sub> and H <sub>2</sub> SO <sub>4</sub>
NiSO <sub>4</sub>	Ni	O <sub>2</sub> and H <sub>2</sub> SO <sub>4</sub>
CuCl <sub>2</sub>	Cu	Cl <sub>2</sub>
AgNO <sub>3</sub>	Ag	O <sub>2</sub> and HNO <sub>3</sub>

electrolytes between platinum electrodes. Often the elements or groups of elements liberated during the passage of the current react with the material of the electrodes. Thus, when a solution of sodium chloride is electrolyzed between a silver anode and a metal cathode coated with silver chloride, metallic silver is formed at the cathode and silver chloride is produced at the anode. Sometimes the changes which take place at the electrodes are far from simple. For instance, Centnerszwer and Drucker<sup>2</sup> have shown that, when solutions of potassium iodide and sodium iodide in liquid sulphur dioxide are electrolyzed, very complex reactions occur at the cathode. It is probable that the alkali metal first separates at this electrode and then reacts with the solvent to form

<sup>1</sup> The theory of the mechanism of the electrolysis of salts, strong acids, and strong bases has been discussed by Verschaffelt, *Natuurw. Tijdschr.*, **8**, 121 (1926).

<sup>2</sup> *Z. Elektrochem.*, **29**, 210 (1923).

hydrosulphite, which subsequently decomposes into thiosulphate and pyrosulphite.

**The Laws of Electrolysis.** Since the passage of electricity through an electrolytic conductor is always associated with a movement of matter and its separation at the electrodes, it is natural to inquire whether there is any relation between the quantity of electricity which passes through a solution and the quantity of matter which separates at the electrodes. The brilliant researches of the celebrated English scientist, Michael Faraday (1791–1867), led to the discovery of this relation, which he expressed in two well-known laws, in 1833. Faraday's first law of electrolysis expresses the fundamental relation existing between the quantity of electricity which passes through a solution and the quantities of the substances which are liberated at the electrodes. This first law states: *the quantities of substances set free at the electrodes are directly proportional to the quantity of electricity which passes through the solution.* Faraday's second law of electrolysis expresses the fundamental relation between the quantities of substances liberated at the electrodes by the same quantity of electricity. The second law states: *the same quantity of electricity sets free the same number of equivalents of substances at the electrodes.* Thus, the quantity of silver liberated at the cathode during the passage of 10 coulombs of electricity through a solution of a silver salt is double that which is deposited when 5 coulombs pass through the solution; and the passage of the same quantity of electricity through solutions of copper chloride, ferric bromide, zinc iodide, and hydrochloric acid sets free quantities of copper, chlorine, iron, bromine, zinc, iodine, and hydrogen which are proportional to their equivalent weights.

The number of *grams* of an element or a group of elements which is *set free* by the passage of 1 *coulomb* of electricity through an electrolytic conductor is called the **electrochemical equivalent** of the element or group. According to Faraday's law, electrochemical equivalents are proportional to chemical equivalents.

It is of interest to calculate the quantity of electricity required to liberate 1 equivalent of an element or group of elements. As has been pointed out, 1 coulomb of electricity sets free 1.118 milligrams of silver from a solution of a silver salt. If, now, we divide the gram-equivalent weight of silver by the electrochemical equivalent of silver, we find that  $107.88/0.001118 = 96,494$  coulombs. This quantity of electricity is called a **faraday** (*F*). In accordance with the second law of electrolysis, the passage of 1 faraday of electricity through an electrolytic conductor will liberate 1 equivalent of some substance at each electrode. If 1 faraday is passed through a solution containing several electrolytes, the sum of the quantities of the different products set free at each electrode will

be unity when expressed in equivalents. Faraday's second law of electrolysis is one of the few exact scientific generalizations. Apparently it has no exceptions. The law is independent of the concentration of the electrolyte; it is valid at all temperatures <sup>1</sup> and for all solvents; <sup>2</sup> and it is applicable to solid electrolytic conductors <sup>3</sup> as well as to solutions or molten salts.

A large amount of investigation has been carried out <sup>4</sup> on the electrolysis of solutions of silver nitrate for the purpose of defining the international ampere, this unit being expressed in terms of the weight of silver deposited by an electric current under rigorously fixed conditions. From the weights of silver and iodine liberated on electrolyzing solutions

TABLE IV  
DETERMINATION OF THE FARADAY

Mean Silver Deposit, mg	Mean Iodine Deposit, mg	Calculated Coulombs		Ratio, Ag : I	Electro-chem. Equiv. of I	Value of the Faraday (I = 126.92)
		From Silver Coulometer	From Cell and Resistance			
4105.82	4829.59	3672.47	.....	0.85013	1.31508	96,511
4104.69	4828.62	3671.45	3671.53	0.85007	1.31518	96,504
4099.03	4822.24	3666.39	3666.55	0.85002	1.31526	96,498
4397.11	5172.73	3933.01	.....	0.85005	1.31521	96,502
4105.23	4828.51	3671.94	3671.84	0.85020	1.31498	96,518
4123.10	4849.42	3687.92	.....	0.85022	1.31495	96,521
4104.75	4828.60	3671.51	3671.61	0.85009	1.31515	96,506
4184.24	4921.30	3742.61	.....	0.85023	1.31494	96,521
4100.27	4822.47	3667.50	3667.65	0.85024	1.31492	96,523
4105.16	4828.44	3671.88	3671.82	0.85020	1.31498	96,519
Arithmetical mean (Nos. 3-10).....				0.85016	1.31505	96,514
Weighted mean (all observations).....				0.85017	1.31502	96,515

<sup>1</sup> Richards, *Proc. Am. Acad. Arts Sci.*, **38**, 409 (1902); *Z. physik. Chem.*, **42**, 621 (1903).

<sup>2</sup> Steele, MacIntosh, and Archibald, *Phil. Trans.*, (A), **206**, 122 (1906); Kahlenberg, *J. Phys. Chem.*, **4**, 349 (1900).

<sup>3</sup> Tubandt and Lorenz, *Z. physik. Chem.*, **87**, 513 (1914); Tubandt and Eggert, *Z. anorg. Chem.*, **110**, 196 (1920).

<sup>4</sup> *Bull. Bur. Standards*, **1**, 1 (1904); **9**, 494 (1912); **10**, 425 (1914); **11**, 220, 555 (1914); Richards, *Proc. Am. Acad. Arts Sci.*, **37**, 415 (1902); **44**, 91 (1908); *J. Am. Chem. Soc.*, **37**, 692 (1915); Smith, Mather, and Lowry, *Natl. Phys. Lab. Rept.*, **4**, 125 (1907).

of silver nitrate and potassium iodide in the same circuit, Bates and Vinal<sup>1</sup> have determined the value of the faraday with an error not exceeding 0.01 per cent. The average of this value and that based on the electrochemical equivalent of silver is 96,505 coulombs. Accordingly the rounded figure **96,500 coulombs** is the value assigned to the faraday.

$$F = 96,500 \text{ coulombs} = 26.8 \text{ ampere-hours}$$

The results of Bates and Vinal's painstaking investigation are summarized in Table IV.

**Coulometers and the Measurement of Quantities of Electricity.** Since the amount of the substances liberated at the electrodes during electrolysis depends upon the quantity of electricity that has passed through a solution of an electrolyte, it is evident that those processes of electrolysis which take place in an unmistakable way, and in which the weight of the liberated substances is easily and readily determined, may be employed for the measurement of quantities of electricity. An electrolytic cell which is used for this purpose is called a **coulometer**.<sup>2</sup> The earliest employment of electrochemical decompositions as a means of measuring quantities of electricity was by Gay-Lussac and Thénard,<sup>3</sup> but it remained for Faraday<sup>4</sup> to enunciate the exact conditions under which these decompositions may be employed for the accurate measurement of quantities of electricity.

Coulometers may be divided into three classes: (a) *weight coulometers*, in which the quantity of electricity is determined by the gain in weight of the cathode of the electrolysis cell, due to the deposition of a metal from a solution of its salt by the current; (b) *volume coulometers*, in which is measured the volume of electrolytic gas (i.e., hydrogen and oxygen in the proportions in which they form water) liberated by the passage of the current through solutions of dilute sulphuric acid, sodium hydroxide, or potassium hydroxide, or the volume of mercury set free during the electrolysis of a suitable mercury salt; and (c) *titration coulometers*, in which the change in concentration, or the amount of a substance set free at one of the electrodes, is determined by titration with a standardized solution. Of these coulometers, the silver (weight) coulometer and the iodine (titration) coulometer are the most accurate, partly on account of the high equivalent weights of silver and iodine. The deposition of 1 gram of silver corresponds to 894.53 coulombs, and the liberation of the same quantity of iodine to 760.33 coulombs.

<sup>1</sup> *Bull. Bur. Standards*, **10**, 425 (1914); *J. Am. Chem. Soc.*, **36**, 916 (1914).

<sup>2</sup> This name was proposed by Richards, *Proc. Am. Acad. Arts Sci.*, **37**, 415 (1902).

<sup>3</sup> *Recherches physico-chimique*, **1**, 12 (1811).

<sup>4</sup> *Exptl. Researches*, **1**, 217 (1834).



(a) *Weight Coulometers.* The silver coulometer has been the subject of a great deal of investigation,<sup>1</sup> because on the accuracy of the measurement of quantities of electricity depend not only the value of the faraday and the definition of the ampere but also the value of the electromotive force of the normal Weston cell, which is employed as a universal standard of electromotive force. The errors in the silver coulometer have been so completely eliminated that the results obtained for the electromotive force of this cell, by investigators in several countries, using three

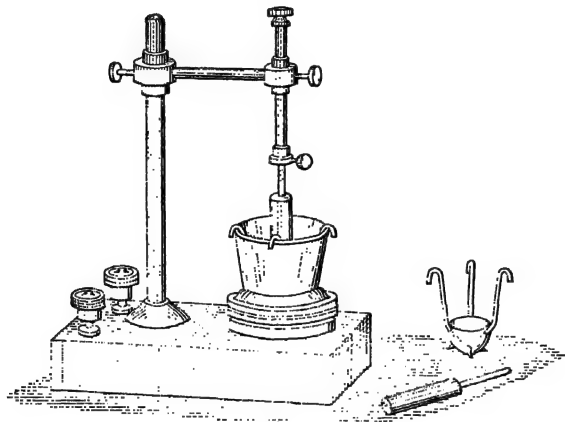


FIG. 6.

types of the coulometer, agree to about one part in one hundred thousand.

In the Kohlrausch form of silver coulometer (Fig. 6), the cathode consists of a burnished platinum dish or crucible, and a small sheet or stick of pure silver (preferably electrolytically deposited) serves as the anode. The active area of the anode should be as large as the size of the coulometer permits. The electrolyte is a 10 to 20 per cent solution of silver nitrate. A small cup of glass or porcelain is hung beneath the anode to catch the anode slime, which is less when the anode has been

<sup>1</sup> Cf. Smith, *Natl. Phys. Lab. Rept.* for 1910, p. 32; Richards, *loc. cit.*; Smith, Mather, and Lowry, *loc. cit.*; Rosa and Vinal, *Bull. Bur. Standards*, **9**, 151 (1913); Rosa, Vinal, and McDaniel, *ibid.*, **9**, 493 (1913); **10**, 475 (1914); Vinal and Bates, *loc. cit.*; Hulett and Vinal, *Bull. Bur. Standards*, **11**, 553 (1915); Vinal and Bovard, *ibid.*, **13**, 147 (1916); Rosa and Vinal, *ibid.*, **13**, 447, 479 (1916); Richards and Anderegg, *J. Am. Chem. Soc.*, **37**, 7, 675 (1915); Oblata, *Proc. Tokyo Math. Phys. Soc.*, **8**, 437 (1916); *ibid.*, **9**, 129 (1917); *ibid.*, **9**, 246 (1918). A new type of silver coulometer has been described by Wartenberg and Schütze, *Z. Elektrochem.*, **36**, 254 (1930).

coated electrolytically with silver. The Smith form <sup>1</sup> of coulometer (Fig. 7) is similar in principle to the one just described, but the construction of the trap is quite different. The anode, *A*, in the form of a disk, is coated with electrolytic silver. The disk is contained in a shallow glass basin, *G*<sub>1</sub> (with a ground edge), supported by a glass rod passing through the center of the disk. A glass cylinder, *G*<sub>2</sub>, with ground ends, fits over the basin and is used to separate the electrolyte into two portions before and after electrolysis. The platinum basin, *P*, serves

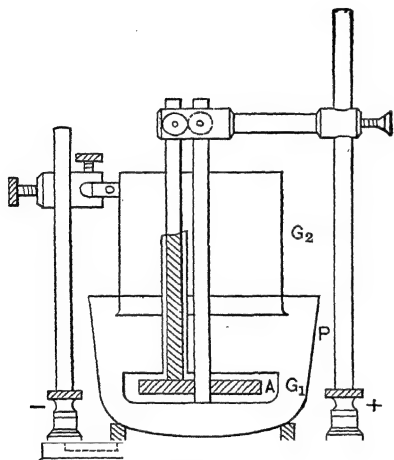
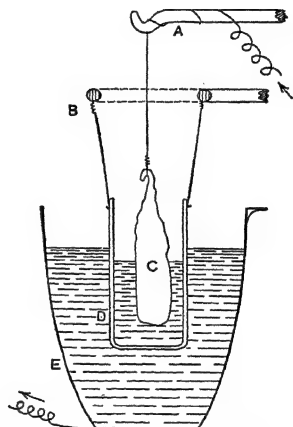


FIG. 7.



Richards Porous Cup Coulometer.  
 A—Glass hook for supporting anode.  
 B—Glass ring for supporting porous cup.  
 C—Silver anode.  
 D—Porous cup.  
 E—Platinum cathode.

FIG. 8.

as the cathode. Instead of the glass trap employed in the Kohlrausch and Smith forms of coulometer, Richards <sup>2</sup> recommends the suspension of the anode in a small porous cylinder (Fig. 8), to prevent disturbing secondary reactions. The extensive investigations carried out at the National Bureau of Standards have shown that these three forms of silver coulometer are highly satisfactory.

The manipulation of the silver coulometer is comparatively simple. The platinum dish is cleaned, dried at 150°, and weighed, after being allowed to cool in a desiccator. The strength of the current passed through the coulometer should not exceed  $\frac{1}{5}$  ampere per square centimeter of anode surface, nor  $\frac{1}{50}$  ampere per square centimeter of cathode

<sup>1</sup> *Natl. Phys. Lab. Rept.* for 1910, p. 32.

<sup>2</sup> *Z. physik. Chem.*, **32**, 336 (1900); cf. Richards and Anderegg, *loc. cit.*

surface. The current should be constant and not more than 1 ampere for not less than 1 hour. As soon as the current flowing through the coulometer is interrupted, the electrolyte is siphoned off and the deposited silver washed with pure, distilled water without delay. The wash waters are siphoned off and tested for silver with a solution of potassium bromide. Several wash waters should be used after potassium bromide gives no further test for silver nitrate. The dish containing the deposit is then dried at  $150^{\circ}$  and weighed.<sup>1</sup>

It is essential that the silver nitrate be of the highest purity; otherwise the weight of the deposit is not independent of the size of the coulometer. This is the so-called volume effect. If the electrolyte is pure, the inclusions within the deposit average only 0.004 per cent of its weight. According to the Bureau of Standards' recommendations,<sup>2</sup> the electrolyte should be free from organic substances and colloids<sup>3</sup> as shown (1) by testing with 1 cc of 0.001 normal potassium permanganate added to 10 cc of an acidified 66 per cent solution of the silver nitrate; (2) by the absence of the "volume effect"; and (3) by the formation of an unstriated deposit.<sup>4</sup> The electrolyte should be neutral or but slightly acid (one part in a million) as tested by methyl red (0.2 per cent in ethyl alcohol) after removal of the silver by neutral potassium chloride. After electrolysis, the electrolyte should be neutral or slightly acid.

For less accurate measurement of quantities of electricity, the *copper coulometer* is often employed. This is similar in principle to the silver coulometer. The electrodes are of pure copper, and the electrolyte consists of 150 grams of crystallized copper sulphate, 50 grams of sulphuric acid (sp. gr. 1.84), and 50 cc of ethyl alcohol<sup>5</sup> in 1000 cc of distilled water. The strength of the current employed should not exceed 0.02 ampere, or fall below 0.002 ampere, per square centimeter of cathode surface. The copper coulometer is inexpensive and easily constructed. It gives results which are sufficiently accurate for many laboratory, and most industrial, purposes.<sup>6</sup> A view of a laboratory form of this coulometer, employed

<sup>1</sup> For further details regarding the operation of the silver coulometer, see Rosa and Vinal, *Bull. Bur. Standards*, **13**, 479 (1916); *Sci. Paper*, No. 285.

<sup>2</sup> Rosa and Vinal, *loc. cit.*

<sup>3</sup> Colloids break up the silver crystals and cause the formation of striated deposits which are too heavy.

<sup>4</sup> Rosa and Vinal (*loc. cit.*) recommend purifying the silver nitrate by crystallization from acid solution and fusion, repeatedly, if necessary.

<sup>5</sup> The addition of ethyl alcohol to the solution minimizes the side reaction,  $\text{Cu}^+ \rightarrow \text{Cu}^{++}$ , at the surface of the electrolyte due to the absorption of oxygen from the air. The alcohol is slowly oxidized to acetone and acetic acid.

<sup>6</sup> Cf. Datta and Dhar, *J. Am. Chem. Soc.*, **38**, 1156 (1916); Oblata, *Proc. Tokyo Math. Phys. Soc.*, **9**, 321 (1918).

for measuring small quantities of electricity, is shown in Fig. 9. In this instrument, the electrolyte is agitated by a stream of small bubbles of carbon dioxide. For the measurement of larger quantities of electricity, a thin sheet copper cathode is placed between two large copper plates which serve as anodes. Since the electrochemical equivalent of copper is 0.0003294, 1 gram of copper deposited on the cathode of the coulometer corresponds to the passage of 3040 coulombs of electricity through the electrolyte.

Some years ago the use of a sodium coulometer, involving the passage of sodium through glass, was suggested,<sup>1</sup> and later an accurate current-measuring instrument of this type was developed and described.<sup>2</sup>

This interesting and convenient coulometer consists of two electrodes immersed in an electrolyte of molten sodium nitrate at 340°, as shown in Fig. 10. The electrodes are evacuated tubes of highly conducting glass<sup>3</sup> containing cadmium in the cathode

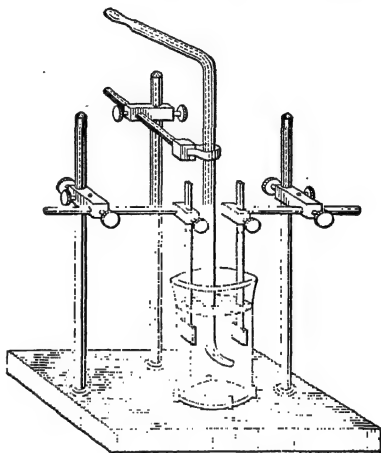


Fig. 9.

and a low-melting-point sodium alloy (3 per cent Na, 97 per cent Cd) in the anode, electrical connection with the metals being made by means of a platinum wire sealed through the glass. On the passage of an electric current, sodium passes into the cathode and out of the anode through the glass. Since the cathode becomes slightly etched during the passage of the current, suggesting electrolytic loss of silicate by the glass, while the anode tube retains its polish, the quantity of current is calculated from the loss in weight of the anode. It has been found that the anodic sodium coulometer yields results which are accurate to 0.01 per cent.

(b) *Volume Coulometers.* In the electrolytic gas coulometer, a 15 per cent solution of sodium or potassium hydroxide is electrolyzed between nickel electrodes. With these electrolytes, the products of electrolysis are hydrogen and oxygen, in the proportion in which they are present in water. If dilute sulphuric acid is used (with platinum electrodes) as the electrolyte, as has been suggested in the past, there is a deficiency of

<sup>1</sup> Burt, *Phys. Rev.*, **27**, 813 (1926).

<sup>2</sup> Stewart, *J. Am. Chem. Soc.*, **53**, 3366 (1931).

<sup>3</sup> "Corning clear, soft lime tubing, No. 015."

oxygen in the electrolytic gas, owing to the formation of some persulphuric acid (see p. 285). The gases are collected and their volume measured at a definite temperature and pressure. Owing to the difficulties of collecting and accurately measuring large volumes of gas, the electrolytic gas coulometer is used only for the measurement of small quantities of electricity.

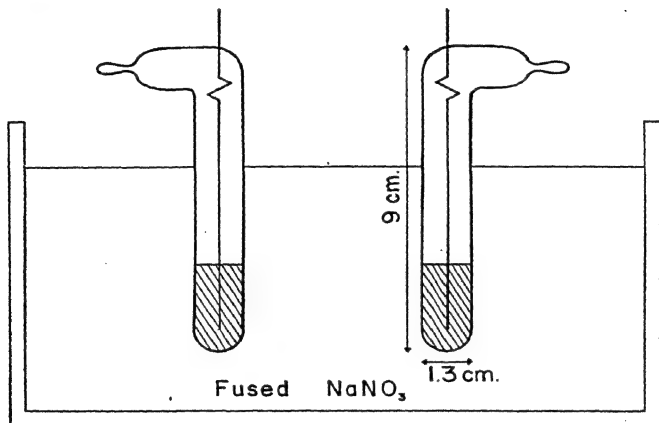


FIG. 10.

Since the passage of 1 faraday of electricity through the electrolytic gas coulometer sets free 1 equivalent each of hydrogen and oxygen, this quantity of electricity will evolve, at 0° and 760 mm pressure,

$$\frac{22.42}{2} \text{ liters H}_2 + \frac{22.42}{4} \text{ liters O}_2 = 16.81 \text{ liters electrolytic gas}$$

Hence, 1-cc of dry electrolytic gas at normal temperature and pressure corresponds to 5.740 coulombs of electricity. The observed volume ( $V$ ) of the gas may be reduced to 0° and 760 mm pressure by means of the formula

$$V_0 = V \cdot \frac{b - h}{760(1 + t/273)} \quad (2)$$

where  $V_0$  is the reduced volume,  $b$  the height of the barometer in millimeters,  $t$  the observed temperature in degrees Centigrade, and  $h$  the tension of the water vapor in millimeters at the temperature  $t$ .

Although in industrial work quantities of electricity are often measured by multiplying the mean current strength, calculated from readings

of an ammeter at frequent intervals, by the time during which the current flows, for more exact, rapid measurement, improved forms of the *Wright coulometer*<sup>1</sup> give good results. This coulometer (Fig. 11) consists of a glass vessel with a circular channel, *A*, which contains a mercury anode. This channel connects directly with a mercury reservoir, *K*. Below *A* is a cathode, *C*, of carbon. A glass collar, *B*, prevents the mercury from being carried over mechanically into the lower part of the vessel. The apparatus is filled with a solution of potassium mercuric iodide (225 grams  $\text{HgI}_2$  and 750 grams  $\text{KI}$  per liter) to a short distance above *B*. Electrical contact is made with *A* and *C* by means of wires sealed in the glass. The mercury is liberated in a very fine stream at *C* and collects in the tube *G*, which is sealed at its lower end. Instead of determining the weight of the mercury set free by the current, its volume is read from the scale, *H*, attached to *G*. This scale may be graduated so as to read ampere-hours directly. When the mercury in *G* rises to a point above the scale, the apparatus is inverted and the mercury allowed to flow back into *K*. By means of a series of shunts, this coulometer may be used with all possible current strengths. An important advantage of the mercury coulometer is the small kilowatt-hour consumption in the measurement of large currents. The accuracy of the instrument is  $\pm 1$  per cent.

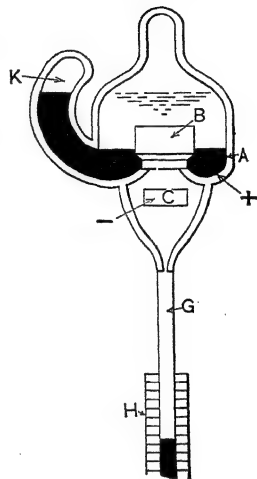


FIG. 11.

(c) *Titration Coulometers*. This form of instrument is convenient for measuring small quantities of electricity, since the errors introduced by washing and drying the cathode are avoided. An iodine titration coulometer, which is free from all errors amounting to more than 0.001 per cent, was designed by Washburn and Bates.<sup>2</sup> The apparatus consists essentially of two vertical limbs connected by a V-tube, and furnished with electrodes of platinum-iridium foil. It is filled with a solution of potassium iodide. During the passage of the current, iodine is liberated in the anode limb, the amount set free being determined subsequently by titration. For less accurate work, the Kistiakowsky silver titration coulometer<sup>3</sup> may be employed. This instrument is accurate within

<sup>1</sup> Cf. Hatfield, *Z. Elektrochem.*, **15**, 728 (1909); Schulte, *ibid.*, **27**, 475 (1921).

<sup>2</sup> *J. Am. Chem. Soc.*, **34**, 1341 (1912). This paper gives a detailed description of the coulometer.

<sup>3</sup> *Z. Elektrochem.*, **12**, 713 (1906).

0.1 per cent when the current strength does not exceed 0.2 ampere and the duration of electrolysis is not over 1 hour. The improved form of the coulometer (Fig. 12) consists of a tube 20–30 cm in length and 20 mm in diameter, which is provided with a stopcock, *S*, at its lower end. The silver anode, *A*, coated with a fresh electrolytic deposit of silver, is sealed into the end of a glass tube containing mercury, through which electrical connection is made with the silver. The tube is filled with a 10 per cent solution of potassium nitrate to a point indicated by the dotted line in Fig. 12. The remainder of the tube is filled with a 7 per cent solution of copper nitrate, to which is added one-fifth of its volume of the potassium nitrate solution. A semi-cylindrical platinum cathode, *C*, dips into the upper solution. During the passage of the current, silver dissolves from the anode: 1 equivalent per faraday. At the conclusion of electrolysis, the solution is run off and the silver which has dissolved is titrated by Volhard's method.

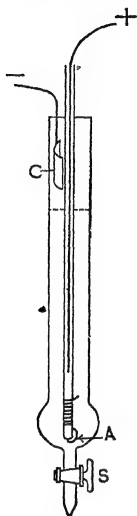


FIG. 12.

**Current Density.** It has been pointed out that, in the electrolysis of salt solutions in weight coulometers, a definite relation between the current strength and the area of the electrodes must be maintained. This relation is called the **current density (C. D.)**, which is defined as the *intensity of the current per unit surface of the electrodes*.

Current density is equal to the ratio of the current strength to the area of the electrodes in square decimeters (or square feet). The terms *anodic* current density and *cathodic* current density denote the intensity of the current per unit area of anode and cathode surface, respectively. A term somewhat analogous to current density is **concentration of current**, by which is meant the ratio of the current strength to the number of cubic centimeters of the electrolyte. Both current density and concentration of current play an important role in electrolysis. Upon the magnitude of these factors often depend the form in which metals are deposited on the cathode, the course of electrolysis, and the nature and quantity of the products liberated or formed at the electrodes. For example, though electrolysis of dilute solutions of sulphuric acid or potassium hydroxide usually yields molecular hydrogen at the cathode, Grubb<sup>1</sup> showed that, when these solutions are electrolyzed with a very high current density, the hydrogen formed at the cathode contains an active component which combines with pure nitrogen to form ammonia. In the electrolytic reduction and oxidation of organic compounds, the

<sup>1</sup> *Nature*, **111**, 671 (1923).

product formed very often depends upon the current density selected (see Chapter XII).

**Current Efficiency.** Although in theory 96,500 coulombs is required to separate 1 equivalent of a substance from a solution, it is usually found that more than this quantity is necessary. That more than the theoretical quantity of electricity is often required in actual practice is not due to the breakdown of Faraday's laws, but to causes such as the following: (1) failure to take into account the separation of more than one substance at either electrode; (2) the mechanical loss of the products of electrolysis; (3) the occurrence of secondary reactions at the electrodes; and (4) current leaks and short circuits. The ratio of the theoretical quantity of electricity to that actually used for the separation of a definite amount of substance is designated **current efficiency** (C. E.). Hence,

$$\text{C. E.} = \frac{\text{Theoretical quantity of electricity}}{\text{Actual quantity of electricity}} \quad (3)$$

$$= \frac{\text{Actual amount of product formed}}{\text{Theoretical amount}} \quad (3a)$$

Current efficiency is a very important factor in many electrochemical processes. In practice, current efficiencies vary considerably. For instance, the electrolytic oxidation of anthracene to anthraquinone is 100 per cent efficient; the electrolytic refining of copper, 95 per cent; alkali-chlorine cells, 50–100 per cent; and the processes for the electrolytic production of metallic sodium and aluminum from their fused salts have a current efficiency of 45 and 70 per cent, respectively.

**Energy Efficiency.** Provided that an electrolytic process could be carried out reversibly and with a current efficiency of 100 per cent, the electrical energy required would be equal to the product of the quantity of electricity used and the theoretical decomposition voltage (see Chapter XI). In practice, however, the *working voltage* is invariably greater than the theoretical voltage, owing both to the voltage required to overcome the ohmic resistance of the electrolyte and to the *irreversibility* of the processes that take place at the electrodes. The **energy efficiency** of an electrolytic process is defined as the ratio

$$\text{E. E.} = \frac{\text{Theoretical quantity of energy}}{\text{Actual quantity of energy employed}} \quad (4)$$

For example, if the theoretical decomposition voltage of an electrolytic process is 1.80 volts and the actual voltage 2.42 volts, then, for a



current efficiency of 85 per cent, the energy efficiency is

$$\frac{1.80}{2.42} \times \frac{85}{100} \times 100 = 63.2 \text{ per cent}$$

Obviously, from the standpoint of economy, the energy efficiency of an electrolytic process is of prime importance in technical work and is of greater significance than the current efficiency. Every effort should be made to raise it as high as possible. This may be effected by decreasing the resistance of the electrolyte, thereby lowering the working voltage.

**The Application of Faraday's Laws to Fused Salts.** So far, we have considered the passage of electricity through only one kind of electrolytic conductor—aqueous salt solutions. The first qualitative experiments on the electrolysis of molten salts were carried out by Sir Humphry Davy,<sup>1</sup> whose researches with potassium nitrate, potassium hydroxide, and sodium hydroxide led subsequently to the isolation of potassium and sodium. Later, Faraday<sup>2</sup> studied the electrolysis of a large number of fused salts. Investigations were also carried out in this field by Hampe,<sup>3</sup> Fousserreau,<sup>4</sup> Bouty and Poincare,<sup>5</sup> Kohlrausch,<sup>6</sup> Graetz,<sup>7</sup> Schultze,<sup>8</sup> Arndt,<sup>9</sup> Lorenz,<sup>10</sup> Arndt and Probst,<sup>11</sup> and others.

The high temperatures necessary to fuse the salts were formerly attained by coal or gas, an air blast being used when required. At present, however, the heat required for the fusion of the salt is usually developed electrically. By means of electrical heating, it is not only easy to maintain the molten electrolyte at a very constant temperature, but, in addition, all disturbances due to flame gases are eliminated.

Two types of apparatus are used for the electrolysis of molten salts, depending on whether a separation of the anodic and cathodic sections is desired. Where a separation of the two sections is not necessary, the simplest type of apparatus consists of a crucible or trough, made of some conducting material such as metal or carbon, which may be employed as the anode or the cathode. The other electrode dips into the molten

<sup>1</sup> *J. Roy. Inst.*, **1801**, 51.

<sup>2</sup> *Phil. Trans.*, **1833**, 507; *Pogg. Ann.*, **31**, 225 (1834).

<sup>3</sup> *Chem. Ztg.*, **11**, 54 (1887); **12**, 1 (1888).

<sup>4</sup> *Ann. chim. phys.*, **5**, 317 (1885).

<sup>5</sup> *Ibid.*, **17**, 52 (1889).

<sup>6</sup> *Wied. Ann.*, **17**, 642 (1882).

<sup>7</sup> *Ibid.*, **40**, 18 (1890).

<sup>8</sup> *Z. anorg. Chem.*, **20**, 333 (1899).

<sup>9</sup> *Z. Elektrochem.*, **12**, 337 (1906).

<sup>10</sup> Numerous papers appearing in the *Z. Elektrochem.*, *Z. physik. Chem.*, and *Z. anorg. Chem.* between 1900 and 1913. *Elektrochemie der geschmolzenen Salze*, 1905.

<sup>11</sup> *Z. Elektrochem.*, **29**, 323 (1923).

salt. If there is no particular reason for making the crucible serve as an electrode, a non-conducting crucible may be employed. One disadvantage of this type of apparatus is that diffusion and vortex motions are not only unretarded, but are accelerated by the gases evolved during electrolysis. The simplest type of apparatus in which the anodic and cathodic sections are separated is that used by Faraday. This consists of a V-tube made of glass, porcelain, or quartz. For laboratory experiments, such a V-tube may be heated conveniently in a small, sheet-iron, asbestos-lined furnace like that shown in Fig. 13. V-tubes made of

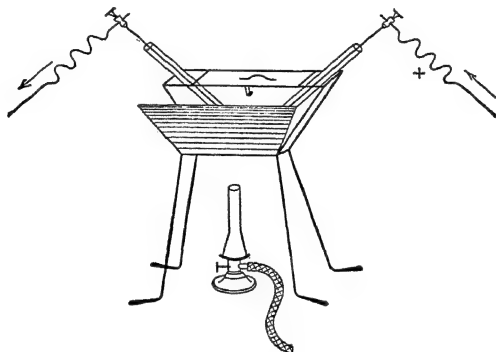


FIG. 13.

Pyrex glass may be employed at temperatures not exceeding  $700^{\circ}$ ; above this temperature, tubes made from quartz or other refractory material must be used. The electrodes employed with these tubes are usually carbon rods having a diameter of 4 to 5 mm. Where a crucible is used, the anodic and cathodic sections may be separated by means of a diaphragm of asbestos board, which does not extend entirely to the bottom of the crucible.

Experiments carried out by Faraday on the electrolysis of molten salts showed that the agreement between the actual and theoretical current yields was nowhere near as close as in the electrolysis of aqueous solutions. Only in a few instances was the current efficiency 99–100 per cent; in many it was as low as 70 per cent. Later investigators obtained even lower values. For example, Bunsen<sup>1</sup> obtained a current efficiency of only 60 per cent in the production of metallic magnesium, and Borchers<sup>2</sup> a current efficiency of 2 to 20, 5, and 1 per cent, respectively, in

<sup>1</sup> *Ann.*, **82**, 137 (1852).

<sup>2</sup> *Pogg. Ann.*, **155**, 633 (1875); see also Brace, *Trans. Am. Electrochem. Soc.*, **37**, 465 (1920).

the preparation of calcium, strontium, and barium. The later investigations of Helfenstein<sup>1</sup> and Richards and Stull<sup>2</sup> showed, however, that Faraday's laws are applicable to molten salts.

In the electrolysis of fused salts, the current efficiency is influenced by one or more of the following factors: cathodic disturbances, anodic disturbances, the distance between the electrodes, the temperature, the current density, and the addition of substances to the electrolyte. It is frequently found that the molten metal liberated at the cathode gives off a metal cloud,<sup>3</sup> which dissolves in the melt, and as this is carried to the anode by diffusion and vortex motion some metal is lost. On the other hand, the halogens, oxygen, and other products liberated at the anode diffuse back to the cathode, and so bring about a decrease in the current efficiency, with respect to the yield of metal. The disturbances which occur at the anode were studied by Arndt and Probst.<sup>4</sup>

The influence of the distance between the electrodes on the current efficiency is illustrated by Helfenstein's data for the electrolysis of lead chloride,<sup>5</sup> in Table V.

TABLE V

INFLUENCE OF DISTANCE BETWEEN ELECTRODES ON CURRENT EFFICIENCY

Current strength = 1 ampere  
 Temperature = 600° C  
 Duration of electrolysis = 40 min

Distance between Electrodes in mm	Cathodic Current Efficiency in Per Cent
2.5	77.50
5	79.23
10	81.26
25	85.35
35	87.63
60	87.55

It will be observed that the current efficiency increases with the distance between the electrodes, owing doubtless to a decrease in the diffusion of the products of electrolysis.

<sup>1</sup> *Z. anorg. Chem.*, **23**, 255 (1900).

<sup>2</sup> *Z. physik. Chem.*, **42**, 621 (1903); cf. also Drossbach, *Z. Elektrochem.*, **45**, 435 (1939).

<sup>3</sup> Cf. Lorenz, *Z. Elektrochem.*, **7**, 277 (1901); Frary and Berman, *Trans. Am. Electrochem. Soc.*, **27**, 509 (1915).

<sup>4</sup> *Z. Elektrochem.*, **29**, 323 (1923).

<sup>5</sup> *Loc. cit.*, p. 266.

Although the relation between current efficiency and temperature is not thoroughly understood, a connection exists between the formation of the metal cloud and the vapor pressure of the metal. The amount of metal in the form of cloud increases with temperature. It is evident, therefore, that loss of metal due to reactions between the metal cloud and the anode products will be greater at higher than at lower temperatures. This loss is increased further, owing to increased diffusion and convection at higher temperatures, in consequence of the decrease in the viscosity of the electrolyte. The influence of temperature on current efficiency is shown by the data <sup>1</sup> in Table VI.

TABLE VI  
ELECTROLYSIS OF MOLTEN LEAD CHLORIDE

Current strength = 1 ampere  
Distance between electrodes = 35 mm  
Duration of electrolysis = 40 min

Temperature, Degrees C	Cathodic Current Efficiency in Per Cent
540	92.14
600	87.65
700	76.58
800	54.87
900	12.31
920	3.15
956 (b.p. of PbCl <sub>2</sub> )	0

The consumption of the metal cloud at the anode is dependent on the current density, since at greater current densities a higher concentration of oxygen or halogen results at the anode. Although the absolute current loss increases with the current density, the former increases less rapidly than the latter. This is shown by the data <sup>2</sup> given in Table VII. The current efficiency as a function of the current density has been discussed by Drossbach,<sup>3</sup> who finds the migration of the metal from the cathode to be due to convection currents set up by anode gases and not to diffusion.

The increase in the current density, however, is limited by the entrance of the so-called anode effect, which results in a great rise in voltage due

<sup>1</sup> Helfenstein, *loc. cit.*, p. 264.

<sup>3</sup> *Z. Elektrochem.*, **40**, 180 (1934).

<sup>2</sup> Helfenstein, *loc. cit.*, p. 265

to the formation of a gas space between the anode and the fused electrolyte.<sup>1</sup> In studying the conditions for the appearance of the anode

TABLE VII

## ELECTROLYSIS OF LEAD CHLORIDE

Distance between electrodes = 35 mm

Temperature = 600° C

Duration of electrolysis = 40 min

Current Strength in Amperes	Cathodic Current Efficiency in Per Cent
5.0	93.36
3.0	96.65
2.0	92.93
1.5	91.05
1.0	87.63
0.5	80.05

effect in the electrolysis of fused chlorides, Heppenstall and Shutt<sup>2</sup> found that at a given temperature the anode effect set in at a definite current density, which increased with rising temperature.

TABLE VIII

## INFLUENCE OF ADDITIONS ON CURRENT EFFICIENCY

## Electrolysis of Lead Iodide

Distance between electrodes = 35 mm

Temperature = 600° C

Current strength = 1 ampere

Duration of electrolysis = 40 min

Per Cent KI	Cathodic Current Efficiency in Per Cent
0	17.8
10.7	45.7
15.3	47.5
26.5	50.5

<sup>1</sup> Cf. Wartenberg, *Z. Elektrochem.*, **32**, 330 (1926).

<sup>2</sup> *Trans. Faraday Soc.*, **20**, 97 (1924).

It is frequently found that the addition of some substance to the electrolyte increases the current efficiency. Thus the addition of potassium iodide increases the current efficiency in the electrolysis of lead iodide, as is shown by Table VIII.<sup>1</sup> On the other hand, the addition of ferric chloride, for example, decreases the current efficiency of the electrolysis of molten salts,<sup>2</sup> owing largely to side reactions.

Recently the theoretical aspects of the factors involved in the electrolysis of fused salts have been discussed by Angel.<sup>3</sup>

### REFERENCES

- LORENZ and KAUFER, *Elektrochemie geschmolzener Salze*, 1909.  
 DROSSBACH, *Elektrochemie der geschmolzener Salzen*, 1939.

### PROBLEMS

1. When an electric current was passed through a dilute solution of sulphuric acid, the hydrogen liberated in 10 minutes measured 100 cc at 17° and 750 mm pressure. Calculate the mean current flowing during the whole time.

2. A current of 2.3 amperes is passed through a solution of copper chloride for 30 minutes. What weight of electrolyte is decomposed?

3. Calculate the current strength it would be necessary to employ in order to decompose 20 grams of zinc bromide (contained in aqueous solution) in 45 minutes.

4. One ampere-hour is passed through solutions of copper sulphate, lead nitrate, silver nitrate, and bismuth chloride. How many equivalents of each metal will be deposited on the cathode?

5. During the passage of 1 ampere-hour through a solution of nickel sulphate, both nickel and hydrogen are liberated at the cathode. If the nickel deposited amounts to 0.0342 equivalent, how many equivalents of hydrogen are set free?

6. In an experiment on the electrolysis of molten lead chloride between electrodes having an area of 40 cm<sup>2</sup>, the following data were obtained:

Current strength, in amperes	2.5	1.5	1.0	0.6	0.25	0.075
Number of coulombs passed through electrolyte.....	4825	12,000	7308	9600	7504	17,020
Grams of Pb liberated at the cathode.....	5	11.5	7	9.25	6.5	10.5

From these data construct a curve showing how the current efficiency changes with the current density.

<sup>1</sup> Lorenz, *Elektrochemie geschmolzener Salze*, p. 37.

<sup>2</sup> Appleberg, *Z. anorg. Chem.*, **36**, 36 (1903).

<sup>3</sup> *Met. Abstracts*, **10**, No. 2, 83 (1939).

## CHAPTER III

### THE THEORY OF ELECTROLYTIC DISSOCIATION

**Osmotic Phenomena.** One of the characteristic properties of a dissolved substance is diffusion, the molecules of the solute moving from regions of high concentration to those of low concentration until the concentration is the same throughout the solution. This process, although much slower on account of the viscosity of the solvent, is similar

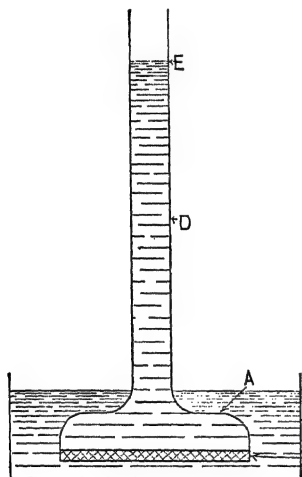


FIG. 14.

to that observed in the study of gases. On the basis of the kinetic molecular hypothesis, the process of diffusion is considered a manifestation of a driving force which, when calculated per unit area, is termed the **osmotic pressure** of the solution. Osmotic pressure may be measured as follows: The tube *A* (Fig. 14), closed at the bottom with a membrane, *B*, which is permeable to molecules of water, but not to those of dissolved substances, is filled with a solution of cane sugar and immersed in a large volume of pure water contained in *C*. Since the membrane prevents the diffusion of the solute molecules, and since equilibrium in the system can result only when the concentrations on the two sides of the membrane are the same, the more

concentrated solution is diluted by the passage of water through the membrane. This causes the solution to rise in the tube *D*, thereby developing an hydrostatic pressure, exerted downwards, which opposes the osmotic pressure. The solution continues to rise in the tube to a height, *E*, when there is equilibrium between the opposing forces. Evidently, the osmotic pressure of a solution, which is a manifestation of the lack of equilibrium between the pure solvent and the solution, is the excess pressure which must be put on a solution to bring it into equilibrium with the solvent. This is numerically equal to the maximum hydrostatic pressure developed in *D*.

Extensive study of dilute solutions has shown that, like gaseous pres-

sure, osmotic pressure obeys the laws of Boyle, Charles, and Avogadro, i.e., the simple gas laws.

It is well known that the vapor pressure ( $p'_1$ ) of a solution is less than that ( $p_1$ ) of the pure solvent at the same temperature. It was found by Raoult<sup>1</sup> empirically, and later demonstrated theoretically, that the relative lowering of the vapor pressure,  $(p_1 - p'_1)/p_1$ , is equal to the mole fraction ( $N_2$ ) of the solute in the solution, i.e.,

$$\frac{p_1 - p'_1}{p_1} = \frac{n_2}{n_1 + n_2} = N_2 \quad (1)$$

where  $n_1$  and  $n_2$  are the number of moles of the solvent and solute, respectively. Equation 1 is known as *Raoult's law*.

By the application of thermodynamics to dilute solutions, van't Hoff showed that the relation between the osmotic pressure ( $P$ ) of a solution and the vapor pressure of the solvent in the pure state and in the solution is given by the expression<sup>2</sup>

$$\ln \frac{p_1}{p'_1} = \frac{MP}{dRT} \quad (2)$$

where  $M$  is the molecular weight of the solvent,  $d$  the density of the solution,  $R$  the gas constant,  $T$  the absolute temperature, and  $\ln$  denotes the natural logarithm.

The left-hand member of equation 2 may be put in the form

$$\ln \frac{p_1}{p'_1} = \ln \left( 1 + \frac{p_1 - p'_1}{p'_1} \right) \quad (3)$$

When the solution is dilute and, therefore,  $(p_1 - p'_1)$  is very small, we may write

$$\frac{p_1 - p'_1}{p_1} = \frac{MP}{dRT} \quad (4)$$

since the logarithm of unity plus a small number is equal to the small number. On combining equations 1 and 4, we obtain the following relation between the osmotic pressure and the composition of the solution:

$$\frac{MP}{dRT} = \frac{n_2}{n_1 + n_2} \quad (5)$$

<sup>1</sup> *Compt. rend.*, **104**, 1430 (1887); *Z. physik. Chem.*, **2**, 372 (1888); *Ann. chim. phys.*, [vi] **15**, 375 (1888).

<sup>2</sup> For the derivation of this expression, the reader is referred to Taylor's *Treatise on Physical Chemistry*, 1930, p. 396, or other textbooks on physical chemistry.



Since, in dilute solutions,  $n_2$  is small in comparison with  $n_1$ , the following approximation suffices:

$$\frac{MP}{RdT} = \frac{n_2}{n_1} \quad (6)$$

Remembering that  $M/d$  is the volume of 1 mole of solvent and rearranging the terms, we reduce equation 6 to

$$P = cRT \quad (7)$$

where  $c$  is the molal concentration of the solute. From the nature of its derivation, it is evident that this limiting form of van't Hoff's equation is applicable only to *dilute* solutions.

Since for dilute solutions in the same solvent at the same temperature  $d$  may be regarded as constant, equation 6 may be written

$$P = k \frac{n_2}{n_1} \quad (8)$$

where  $k$  is a constant.

Another property of a solvent which is influenced by the presence of a solute is its freezing point, the solid solvent separating from a solution at a lower temperature than when in the pure state. The magnitude of the lowering of the freezing point of the solvent produced by the presence of the solute varies with the concentration of the solute, the relation being given by the Raoult-van't Hoff equation <sup>1</sup>

$$\Delta = \frac{RT^2}{\rho} \frac{n_2}{n_1 + n_2} \quad (9)$$

where  $\Delta$  is the lowering of the freezing point,  $\rho$  is the molal heat of fusion of the solid solvent at the absolute temperature  $T$ , and the other quantities have their previous significance. For dilute solutions we may write

$$\Delta = k' \frac{n_2}{n_1} \quad (10)$$

where the constant  $k'$  is equal to  $RT^2/\rho$ . For a large number of substances, such as sugar, alcohol, mannite, and urea, it has been found that the lowering of the freezing point of water is  $1.858^\circ$  for every formula weight of solute present in 1000 grams of water. On the other hand, the majority of inorganic salts, many organic salts, acids, and bases produce freezing-point depressions which exceed  $1.858^\circ$ , or even

<sup>1</sup> For the derivation of this equation, the reader is referred to Taylor's *Treatise on Physical Chemistry*, 1930, pp. 363-5, or to other textbooks on physical chemistry

two, three, or more times this value. Those substances which give abnormal freezing-point depressions also produce osmotic pressures which are higher than the values calculated by equation 8.

In his theory of solutions, van't Hoff designated by the symbol  $i$  the ratio of the osmotic pressure or freezing-point depression (or other colligative property, i.e., a property which depends on the number of

TABLE IX  
VALUES OF THE MOLE NUMBER

Substance	Concentration (Molal)		
	0.1	0.05	0.01
MgSO <sub>4</sub>	1.32	1.42	1.62
KIO <sub>3</sub>	1.77	1.83	1.91
KNO <sub>3</sub>	1.78	1.84	1.90
KClO <sub>3</sub>	1.80	1.85	1.91
KBrO <sub>3</sub>	1.81	1.85	1.92
NaNO <sub>3</sub>	1.83	1.86	1.90
KCl	1.86	1.89	1.94
NH <sub>4</sub> Cl	1.86	1.88	1.93
KOH	1.87	1.93	1.98
NaCl	1.88	1.89	1.94
LiCl	1.90	1.91	1.94
HNO <sub>3</sub>	1.90	1.91	1.96
HCl	1.92	1.93	1.98
CdI <sub>2</sub>	1.45	1.80	2.19
CdCl <sub>2</sub>	2.21	2.38	2.58
H <sub>2</sub> SO <sub>4</sub>	2.22	2.32	2.58
Pb(NO <sub>3</sub> ) <sub>2</sub>	2.30	2.45	2.70
BaCl <sub>2</sub>	2.58	2.64	2.76
K <sub>3</sub> Fe(CN) <sub>6</sub>	....	....	3.60
K <sub>4</sub> Fe(CN) <sub>6</sub>	3.32	3.54	

molecular species present in solution) produced by 1 formula weight of a substance to that produced by 1 formula weight of a perfect solute. This ratio, called the **mole number** or the **van't Hoff factor** of the solute, is the number of molecular species resulting from 1 formula weight of solute. Hence, by multiplying  $n_2$  in equations 8 and 10 by  $i$ , we obtain the expressions

$$P = k \cdot \frac{i \cdot n_2}{n_1} \quad (11)$$

$$\Delta = k' \cdot \frac{i \cdot n_2}{m} \quad (12)$$

which for all solutes yield values of osmotic pressures and freezing-point depressions that agree with those determined by experiment. For substances like cane sugar, the value of  $i$  is unity. Values of  $i$  which show the influence of a number of solutes on the freezing-point depression of water at concentrations of 0.1, 0.05, and 0.01 molal<sup>1</sup> are shown in Table IX.

**Gaseous Dissociation.** A phenomenon similar to the phenomena just discussed was observed as early as 1857 by Deville and Troost. In their experiments with gaseous ammonium chloride, they found that the pressure of the gas at 350° and 1040° was about double the value calculated by means of the general gas equation. This behavior was shown by Pebal<sup>2</sup> to be due to the molecules of ammonium chloride breaking up into molecules of ammonia and hydrochloric acid. This phenomenon of the breaking up of gaseous molecules into simpler molecules is termed *dissociation*. Other gases have been found to dissociate under certain conditions. Since, at a definite temperature and volume, the pressure of a gas depends on the number of molecules present, it is evident that, if the number of molecular species is increased by dissociation, the pressure will be increased correspondingly. Thus, if ammonium chloride is completely dissociated into its component molecules, the observed pressure will have double the value calculated on the assumption that the gas consists of undissociated molecules.

**Electrolytic Dissociation.** It is noteworthy that those substances which, when dissolved, give rise to abnormal osmotic pressures and freezing-point depressions are the same substances which, in solution, conduct the electric current. In order to explain this behavior, the Swedish physicist, Svante Arrhenius, in 1887, formulated a *theory of electrolytic dissociation*. According to Arrhenius' theory, the molecules of those substances which have been termed electrolytes break up into positively and negatively electrified particles, called **ions**, when dissolved in water. This **electrolytic dissociation**, or **ionization**, readily explains the abnormal osmotic effects produced by electrolytes, since it results in an increase in the number of particles of solute present in solution, and also the phenomenon of electrolysis. Since under the influence of an electric field the ions are found by *direct observation* to move in opposite directions, it is inferred that those which move towards the cathode, called **cations**, are positively charged and those which travel towards the anode, called **anions**, are negatively charged. When a cation comes in contact with the cathode, its electric charge is neutralized and it is liberated as an atom or a group of atoms. The same processes

<sup>1</sup> Noyes and Falk, *J. Am. Chem. Soc.*, **32**, 1011 (1910).

<sup>2</sup> *Ann.*, **123**, 199 (1862).

take place at the anode with respect to the anion. Since the electricity which is consumed at the electrodes by this discharge of ions is immediately replaced by a further quantity from the battery or generator in the circuit, a current of electricity flows through the circuit.

The theory of electrolytic dissociation does not assume that *all* the molecules in solution are dissociated. From the values of the mole number given in Table IX, it would appear as though only a fraction of the molecules is dissociated and that this fraction increases as the concentration of the electrolyte becomes less. Accordingly, for an electrolyte which forms two ions, it was assumed that all the molecules are dissociated only when the mole number has a value of 2; for one which yields three ions, only when the mole number is 3. If we represent the **degree of dissociation** of an electrolyte, or the fraction of each formula weight dissociated into ions by  $\alpha$ , and the number of ions into which each molecule dissociates by  $\nu$ , then

$$\begin{aligned} i &= (1 - \alpha) + \nu\alpha \\ &= 1 + (\nu - 1)\alpha \end{aligned}$$

whence

$$\alpha = \frac{i - 1}{\nu - 1} \quad (13)$$

By means of equation 13, the degree of dissociation of an electrolyte may be calculated from osmotic-pressure, freezing-point, or vapor-pressure data. In Chapter V it will be shown that the degree of dissociation may be determined also from measurements of electrolytic conductance. Table X shows the percentage dissociation ( $100\alpha$ ) of several electrolytes at different normal concentrations. These values have been calculated from freezing-point and conductance data.<sup>1</sup>

The idea that electrically charged particles exist in solutions of electrolytes did not originate with Arrhenius. The foundation for this conception was laid by Faraday, who assumed that the electric current was carried through an electrolytic conductor by charges of positive and negative electricity associated with definite material bodies, traveling in opposite directions. He stated: "I propose to distinguish such bodies by calling those *anions* which go to the anode of the decomposing body; and those passing to the cathode, *cations*; and when I have occasion to speak of these together, I shall call them *ions*. Thus chloride of lead is an *electrolyte*, and when *electrolyzed* evolves two *ions*, chlorine and lead, the former being an *anion* and the latter a *cation*."<sup>2</sup> The results of later

<sup>1</sup> Noyes and Falk, *J. Am. Chem. Soc.*, **34**, 485 (1912).

<sup>2</sup> *Experimental Researches*, 1834.

researches by Hittorf<sup>1</sup> and Kohlrausch<sup>2</sup> indicated that an electrolyte is dissociated in solution, although neither reached this conclusion. As a result of an investigation carried out to determine the energy required to electrolyze solutions of silver nitrate,<sup>3</sup> Clausius made the assumption

TABLE X

Concentration (Normal).		0.005	0.05	0.1
Electrolyte	Method	Percentage Dissociation		
KCl	F. P.	96.3	88.5	86.1
	Cond.	95.6	88.9	86.0
NaCl	F. P.	95.3	89.2	87.5
	Cond.	95.3	88.2	85.2
LiCl	F. P.	94.4	91.2	90.1
	Cond.	94.9	87.8	84.6
KBr	F. P.	....	88.9	86.3
	Cond.	95.5	88.8	85.9
NaIO <sub>3</sub>	F. P.	93.9	84.2	77.3
	Cond.	93.9	84.2	80.1
HCl	F. P.	99.1	93.3	91.7
	Cond.	98.1	94.4	
MgSO <sub>4</sub>	F. P.	69.4	42.0	32.4
	Cond.	74.0	50.6	44.9
Pb(NO <sub>3</sub> ) <sub>2</sub>	F. P.	89.0	72.4	64.9
	Cond.	88.6	70.8	63.5

that electrolytes are dissociated in solution, when he concluded that "the supposition that the constituents of the molecule of an electrolyte are united and exist in a fixed and orderly arrangement is wholly erroneous." To Arrhenius, however, are due the credit and honor of having developed the ideas of Clausius and Faraday, and of having erected a fundamental, quantitative hypothesis of electrolytic dissociation of

<sup>1</sup> *Pogg. Ann.*, **89**, 177; **98**, 1; **106**, 377, 513 (1853-1859).

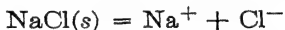
<sup>2</sup> *Göttinger Nachrichten*, 1876, p. 213; *Wied. Ann.*, **6**, 145 (1879); **11**, 653 (1880).

<sup>3</sup> *Pogg. Ann.*, **101**, 338 (1857).

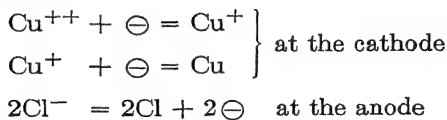
electrolytes upon their conductances, osmotic pressures, freezing points, additive properties, and catalytic actions.

Since solutions of electrolytes are always electrically neutral, Arrhenius' theory assumes that dissociation results in the formation of equivalent quantities of cations and anions. The magnitude of the charges carried by these ions may be ascertained from a study of electrolysis. Inasmuch as the passage of 1 faraday of electricity through a solution of an electrolyte liberates 1 gram equivalent of an ion or ions at each electrode, it follows that 1 gram equivalent of an anion carries 96,500 coulombs of negative electricity, and 1 gram equivalent of a cation is associated with the same quantity of positive electricity. Accordingly, the quantity of electricity carried by any gram ion is  $zF$ , where  $z$  is the valence of the ion. Since 1 gram ion contains  $6.02 \times 10^{23}$  (Avogadro's number,  $N$ ) ions, a single ion must carry a charge of  $96,500/6.02 \times 10^{23} = 1.60 \times 10^{-19}$  coulomb of positive or negative electricity, or a simple multiple,  $z$ , of this quantity. This ultimate quantity ( $1.60 \times 10^{-19}$  coulomb or  $4.80 \times 10^{-10}$  esu) of negative electricity is the charge carried by the **electron**, a particle having a mass 1844 times less than that of the hydrogen atom.<sup>1</sup> The corresponding quantity of positive electricity is that associated with the hydrogen ion or **proton**. The positive electron or **positron** has been discovered,<sup>2</sup> with a mass but little different from that of the electron.<sup>3</sup>

It is customary to denote each faraday of positive electricity by a *plus* sign (+ or  $\oplus$ ), and the corresponding amount of negative electricity by a *minus* sign (− or  $\ominus$ ). Thus the electrolytic dissociation of solid sodium chloride and copper sulphate into their respective ions may be represented



The chemical and electrical changes which take place during electrolysis may be expressed by **electrochemical equations**. For example, the equations for the electrolysis of a solution of copper chloride between platinum electrodes, are



<sup>1</sup> Cf. Dunnington, *Phys. Rev.*, [ii], **43**, 404 (1933).

<sup>2</sup> Anderson, *Science*, **76**, 238 (1932); Blackett and Occhialini, *Proc. Roy. Soc.*, **A139**, 699 (1933).

<sup>3</sup> Anderson, *Phys. Rev.*, [ii], **43**, 491 (1933); [ii], **44**, 406 (1933).

The phenomenon of electrolytic dissociation is not confined to aqueous solutions. Since, as we have seen in the preceding chapter, solutions of electrolytes in solvents other than water conduct the electric current, it may be inferred that the electrolytes are dissociated in these solvents. Substances which give conducting non-aqueous solutions are not necessarily dissociated in water. Water, however, is much more effective in bringing about dissociation than most other solvents. (The relations between dissociating power and other properties of solvents will be discussed in the next chapter.) Since molten salts exhibit the same phenomena which led to the formulation of the theory of electrolytic dissociation for solutions of electrolytes, it may be concluded that ions are present also in this type of electrolytic conductor.<sup>1</sup> Confirmation of this conclusion is due to Meyer and Heck,<sup>2</sup> whose results of measurements of the refraction of molten sodium nitrate indicate that this salt exists largely as ions at high temperatures.

**Modern Theory of Electrolytic Dissociation.** In its modern form, the theory of electrolytic dissociation assumes that in solution the vast majority of salts, and the strong acids and bases, exist entirely as ions. This hypothesis of *complete* dissociation is supported by evidence obtained from the X-ray study of crystals of electrolytes. It has been found that in the crystalline state these substances do not consist of molecules, in the usual sense, but of electrically charged atoms, or groups of atoms, arranged in a space lattice. Thus the structural units of solid sodium fluoride, for example, are positively charged sodium atoms and negatively charged fluorine atoms, so arranged in the lattice that each sodium atom is equidistant from six fluorine atoms and each fluorine atom is equidistant from six sodium atoms. The conducting power of the crystal is small, however, since free movement of the charged atoms is prevented by the large crystal forces. When a solid electrolyte is placed in water, or heated to its melting point, the crystal forces are weakened and the crystal simply disintegrates into the *pre-existing* electrically charged particles or ions.

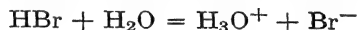
Very frequently the ions do not exist in solution simply as the charged constituents of the electrolyte. It is generally accepted that certain ions are solvated, or associated with molecules of the solvent. An ion and a solvent molecule may form a definite compound, and, with solvents possessing strongly polar molecules (e.g.,  $\text{H}_2\text{O}$  and  $\text{NH}_3$ ; cf. Chapter IV), the ions may associate with an additional quantity of the solvent, owing to the attraction resulting from the charge of the ion and the electric moment of the solvent molecules. It is very improbable, for example,

<sup>1</sup> Cf. Lorenz, *Z. physik. Chem.*, **70**, 230 (1910); **79**, 63 (1912).

<sup>2</sup> Z. *Elektrochem.*, **28**, 21 (1922); *Z. physik. Chem.*, **100**, 316 (1922).

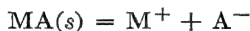
that the bare proton (unsolvated hydrogen ion) exists in solution to any appreciable extent. What is usually termed the "hydrogen ion" is in aqueous solution the oxonium ion,  $\text{H}_3\text{O}^+$ , bearing the same relation to oxygen as the ammonium ion does to nitrogen.

The dissociation of the strong acids is somewhat different from that of salts. There is little or no evidence that hydrogen bromide, for example, is appreciably ionized in the undissolved state. In water, however, it breaks up into ions, presumably as the result of a reaction between its molecules and those of the solvent, to form oxonium bromide, thus:



This supposition is supported by results obtained by Bagster and Cooling,<sup>1</sup> who found that, although a solution of dry hydrogen bromide in liquid sulphur dioxide was almost a non-conductor, the addition of a small quantity of water (which is also a non-conductor) caused conductance with liberation of hydrogen at the cathode, while water was carried from the anode to the cathode and deposited there. From this behavior, and from the fact that the weight of water deposited at the cathode was equivalent to the weight of silver deposited in a coulometer placed in series with the electrolysis cell, it must be concluded that a true oxonium ion is formed. During electrolysis this ion loses its positive charge at the cathode and breaks down into hydrogen and water.

Since it is assumed that the dissolution of a solid salt, MA, results in complete dissociation,



it might be expected that the mole number, as determined by the measurement of some colligative property, would be 2. That its value is usually less than this is shown by the data of Table IX for salts of this type. It must be remembered, however, that in solution electrical forces are still exerted between the ions, although they are much weaker than in the crystalline state. As a result of these interionic attractions, even in dilute solution the ions are not uniformly distributed throughout the solution but each ion has in its immediate vicinity an excess of ions of opposite electrical charge.<sup>1</sup> This "ion atmosphere" exerts a restraint on the oppositely charged ion and decreases its independence of movement. The strength of the interionic attractive forces is greater the closer the ions are to one another, i.e., the more concentrated the solution, and it may be sufficiently great to cause oppositely charged ions to approach each other so closely that they cease to be independent and form for a time an ion pair. Since this is equivalent to a decrease in dissociation,

<sup>1</sup> *J. Chem. Soc.*, **117**, 693 (1920).



even though ionization is complete, the mole number would have a value less than that corresponding to complete dissociation. As the concentration of the electrolyte is decreased, the distance between the ions increases, and in very dilute solution they are so far apart that the interionic forces are negligible. According to Bjerrum,<sup>1</sup> oppositely charged ions cannot form ion pairs, and so behave like undissociated molecules, unless they are separated by less than a definite distance.

There is no reliable method for the determination of the degree of dissociation of most salts, and strong acids and bases. Indeed, it is doubtful whether the degree of dissociation has any clear significance for these types of electrolytes, since for them it cannot be defined without ambiguity. Notwithstanding the fairly close agreement between the results of two independent methods given in Table X, these values for the degree of dissociation are much too low. Equation 13 gives incorrect values because the ions do not behave as ideal solutes; the values for the degree of dissociation obtained by the conductance method are inaccurate on account of restraints exerted on the ions by the electrical forces. However, these values furnish a rough approximation of the concentration of "free" ions in solution which is useful for some purposes.

The inability to separate the dissociated components of an electrolyte, as in gaseous dissociation, might be cited as an objection to the theory of electrolytic dissociation. When it is remembered, however, that the ions of an electrolyte carry large charges of positive and negative elec-

tricity, it is obvious that the separation of the anions from the cations must be attended with great difficulty. Indeed, if 1 milliequivalent of an anion were to be removed from a solution, the solution would be left with an excess of 96.5 coulombs of positive electricity, a quantity sufficient to give to a large flask covered with tinfoil a potential of about  $10^{12}$  volts. However, a partial separation of the two kinds of ions was

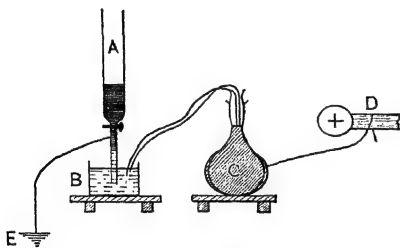


FIG. 15.

actually achieved by Ostwald and Nernst,<sup>2</sup> in the following manner: A glass tube, A (Fig. 15), provided with a tap and drawn out at one end so as to form a capillary, was filled with mercury. The capillary was immersed in dilute sulphuric acid contained in a glass vessel B, and the mercury adjusted in such a way that one-half of the capillary was filled with the acid. The vessel B was connected by means of a damp thread

<sup>1</sup> *Svensk Kem. Tidskr.*, **38**, 2 (1926).

<sup>2</sup> *Z. physik. Chem.*, **3**, 120 (1889).

with a second solution of sulphuric acid contained in an insulated flask, *C*, covered with tinfoil. On giving the tinfoil a positive charge from an electrical machine, *D*, it was found that bubbles of hydrogen were given off at the junction of the acid with the mercury in *A*, when the mercury was connected to earth through the platinum wire *E*. The liberation of gaseous hydrogen was due to the fact that the positively charged tinfoil of the flask attracted the negatively charged sulphate ions, while the positively charged hydrogen ions were repelled to the earth-connected mercury, where they gave up their positive charges and became atoms of hydrogen.

Later Tolman<sup>1</sup> demonstrated the existence of free ions by whirling aqueous solutions of a number of iodides in tubes in a very powerful centrifugal machine. He found that the extreme ends of the tubes acquired a negative charge, presumably due to an accumulation of the heavier iodine ions, while the opposite ends of the tubes became positively charged, probably due to a slight excess of the lighter cations. This result furnishes a direct and almost absolute proof that some degree of dissociation must exist in aqueous solution, and that the positive and negative ions can move relatively to one another.

**Classification of Electrolytes.** Electrolytes may be divided broadly into two groups: (1) the **strong electrolytes** and (2) the **weak electrolytes**. To the first group belong the strong acids and bases and most of the soluble combinations of metallic cations and inorganic anions. To the second group belong the weak inorganic acids, the majority of organic acids, the phenols, the primary to tertiary substituted amine bases, and a number of inorganic salts, such as  $\text{HgCl}_2$ ,  $\text{Hg}(\text{CN})_2$ ,  $\text{FeF}_3$ , and  $\text{Fe}(\text{SCN})_3$ . In addition to these two groups of electrolytes, a third classification, the **transition electrolytes**, which includes a number of acids of intermediate strength, is sometimes used.

Electrolytes which dissociate into two ions, e.g., potassium chloride or magnesium sulphate, are termed **binary electrolytes**; those which form three ions, e.g., barium chloride, are called **ternary electrolytes**; and those which yield four ions, e.g., aluminum chloride, are designated **quaternary electrolytes**. Binary electrolytes may be either **uniunivalent** ( $\text{NaCl}$ ) or **bivalent** ( $\text{CuSO}_4$ ); ternary electrolytes, **unibivalent** ( $\text{K}_2\text{SO}_4$ ); quaternary electrolytes, **terunivalent** ( $\text{FeCl}_3$ ), etc.

**The Nature of the Ions.** The determination of the nature of the ions which result from the dissociation of an electrolyte is important. Very often it is obvious that the ions are the same substances which separate at the electrodes during electrolysis, but this is not always true. For

<sup>1</sup> *Proc. Am. Acad. Arts Sci.*, **46**, 109 (1910); cf. also Hevesy and Zechmeister, *Ber.*, **53**, 412 (1920); MacInnes, *Ann. N. Y. Acad. Sci.*, **43**, 243 (1942).

example, when a solution of sodium chloride is electrolyzed, hydrogen, and not sodium, is observed at the cathode. It is quite obvious, however, that sodium chloride can dissociate only into a sodium ion and a chlorine ion, and that the products liberated at the electrodes during electrolysis result from the decomposition of the water. Sometimes reactions take place at the electrodes between the discharged ions and the electrodes or the solvent.

Hittorf showed that the nature of the ions may be ascertained by determining the changes in concentration which occur in the neighborhood of the electrodes during electrolysis. The majority of salts dissociate into the cation,  $M^+$  (or  $M^{++}$ , etc.), of the base, and the anion,  $A^-$  (or  $A^{--}$ , etc.), of the acid, from which they are formed. With the exception of the ions of salts of organic bases and those of a few of the type of ammonium salts, the cations of salts consist essentially of charged atoms of metallic elements.

Although it had long been known that all acids contained hydrogen, it was not entirely clear just what determined whether a compound containing hydrogen was an acid or not. In the light of the theory of electrolytic dissociation, acids are those substances which, in solution, yield hydrogen ions. This explains why such different substances as hydrochloric, sulphuric, and phosphoric acids all turn blue litmus red: the change is effected not by chemically different molecules but by hydrogen ions produced by the different molecules. Bases are those substances which give rise to hydroxyl ions in solution. The following are the more important properties of the hydrated hydrogen (oxonium) ion (and, therefore, of acids):

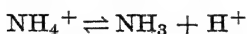
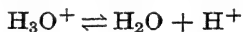
1. Hydrogen ions change the color of certain substances called indicators.
2. They accelerate, catalytically, the velocity of certain reactions, for example the inversion of cane sugar.
3. They dissolve certain metals.
4. They have a sour taste.
5. They neutralize the characteristics of hydroxyl ions.
6. They are a determining factor in many physiological processes, fermentation, etc.

The following are the more important characteristics of the hydroxyl ion (and, therefore, of bases):

1. Hydroxyl ions change the color of certain indicators, but in the reverse sense to that by hydrogen ions.
2. They accelerate, catalytically, the velocity of the condensation of acetone to diacetone alcohol, mutarotation, and the saponification of esters.

3. They have a bitter, brackish taste.
4. They destroy the characteristics of the hydrogen ions.

The foregoing definitions of acid and base were broadened by Brönsted,<sup>1</sup> who defined an acid as a source of protons ( $H^+$ ) or a proton donor, and a base as a proton acceptor or any substance which can unite with protons. According to these later definitions the oxonium ion, the cations of weak bases, and the undissociated molecules of weak acids are acids; the hydroxyl ion, the anions of weak acids, and weak bases are bases. The following are examples of the types of acids just mentioned:



Considering the first of these equations,  $H_3O^+$  is the "conjugate acid" of the base  $H_2O$ , and  $H_2O$  is the "conjugate base" of the acid  $H_3O^+$ . The same terminology is applied to the substances represented in the other two equations.

**Some Explanations Afforded by the Theory of Electrolytic Dissociation.** In addition to accounting for the abnormal osmotic behavior and the conductance of electrolytes, the theory of electrolytic dissociation afforded simple explanations of many other phenomena; the impressive verification of its consequences rapidly won it many supporters.

The immediate formation of a precipitate of silver chloride on the addition of silver nitrate to solutions of dissimilar chlorides is due to a union of silver and chlorine ions. On the other hand, this reaction does not take place with chlorates and perchlorates, substances which contain chlorine, but which do not yield chlorine ions. In the same way the theory accounts for the fact that sulphates are precipitated by solutions of barium salts. This behavior was inexplicable on the basis of older chemical theories. Since the majority of inorganic salts yield ions when dissolved in water, ionic reactions are employed in analytical chemistry and, in consequence, a short, concise system of inorganic analysis has been developed.<sup>2</sup> The theory of electrolytic dissociation furnished analytical chemistry with a leading principle it lacked before. On the other hand, any system of organic analysis must necessarily be complicated, since the majority of the several hundred thousand organic compounds are non-electrolytes.

Chemical activity is, in many instances, a result of electrolytic dissociation, reactions taking place between ions more readily and rapidly,

<sup>1</sup> *Chem. Revs.*, **5**, 321 (1928).

<sup>2</sup> E.g., by A. A. Noyes and his co-workers.

and with the accompaniment of smaller energy changes, than between molecules. Although ionic reactions in aqueous solution are numerous and familiar, the only other solvent in which these reactions have been extensively studied is liquid ammonia.<sup>1</sup> Since, however, many substances are dissociated in non-aqueous solvents, it may be inferred that ionic reactions also occur in solutions in these solvents. In many respects, reactions in fused salts resemble ionic reactions in aqueous solution.

The theory of electrolytic dissociation affords an explanation of the additive nature of many physical properties of dissolved substances, such as color, density, refractivity, and conductance. Since the properties of ions must be constant so long as they remain the same, their additive nature is a necessary consequence.

The well-known contraction in volume which occurs when salts are dissolved in water is in harmony with the dissociation theory, for, as Drude and Nernst<sup>2</sup> first pointed out, a decrease in volume should result from the action of the electrostatic field, due to the ions,<sup>3</sup> on the molecules of the solvent.

For equivalent solutions, it was found<sup>4</sup> that the difference between the density of sodium chloride and potassium chloride is equal to that of the corresponding nitrates. Similarly, the difference between the density of ammonium chloride and ammonium nitrate is the same as that of the corresponding sodium or potassium salts. Heydweiller's measurements of the density of aqueous solutions of salts<sup>5</sup> show that the percentage change in the density per gram equivalent of dissolved electrolyte is an additive property of the ions.

The additive nature of conductance will be considered in a later chapter.

**Some Problems and Achievements.** It was conceded from the beginning that the theory of electrolytic dissociation raised many difficulties the solution of which would require a vast amount of experimental investigation. Some of these problems were the precise determination of the extent to which electrolytes break up into ions; the mechanism of dissociation, "which involved investigations with solvents other than water; the question of 'solvation' of the ions [i.e., union of the ions with the solvent]; the electromotive activity of the ions; the chemical activity

<sup>1</sup> Cf. Franklin and Kraus, *Am. Chem. J.*, **23**, 277 (1900); and subsequent papers by Kraus and his co-workers in the *J. Am. Chem. Soc.*; Franklin, *The Ammonia System of Compounds*, 1935.

<sup>2</sup> *Z. physik. Chem.*, **15**, 79 (1894).

<sup>3</sup> According to Drude and Nernst's calculations, the mean field of the ions in a normal solution amounts to more than 20,000 volts.

<sup>4</sup> Cf. Valson, *Compt. rend.*, **73**, 441 (1871); **77**, 806 (1873).

<sup>5</sup> *Ann. Physik*, **30**, 873 (1910); **37**, 739 (1912).

of the ions; and the relation between color (more generally absorption spectra) and constitution of electrolytes. All these problems have now been brought much nearer solution, and some of them have been practically solved. Among the outstanding achievements in this field may be mentioned (1) Nernst's theory of electromotive force; (2) the enunciation by J. J. Thomson and Nernst independently (1893) of the rule that the ionizing power of a solvent is closely connected with its dielectric constant; (3) the comprehensive investigations of Walden on the connection between ionizing power and other properties of solvents; (4) the admirable experimental investigations of A. A. Noyes, Washburn, and their collaborators in America on the exact degree of ionization of strong electrolytes."<sup>1</sup> These achievements will be discussed subsequently.

Although the electrolytic dissociation theory of Arrhenius survived many years of experimental investigation and criticism, during which period it stimulated research and contributed markedly to the progress of chemistry, physics, and other sciences, the investigator ultimately had to face seriously the problem of its difficulties and defects.<sup>2</sup> Some of these we shall meet as we proceed (particularly in Chapters XIII and XV). During this century the theory has been modified, as already pointed out, largely by Sutherland, Milner, Debye and Hückel, and Onsager. In its original form it is completely valid only for weak acids and bases and a few salts. In solutions of these electrolytes, ions and undissociated molecules exist in equilibrium.

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- GETMAN and DANIELS, *Outlines of Physical Chemistry*, 1943.  
H. S. TAYLOR, *Treatise on Physical Chemistry*, 1930, Chapter VII.

## PROBLEMS

1. The freezing points of 0.02 molal solutions of lithium chloride, nitric acid, and potassium ferricyanide are, respectively,  $-0.0717^{\circ}$ ,  $-0.0723^{\circ}$ , and  $-0.1239^{\circ}$ . Calculate the mole number of these substances at this concentration.
2. From the values of the mole numbers of sodium chloride, lead nitrate, and potassium ferrocyanide in 0.1 and 0.05 molal solutions (Table IX), calculate the fraction of the salt dissociated to which these values of  $i$  would correspond if the ions acted as perfect solutes.
3. At  $0^{\circ}$  the degree of dissociation of potassium chloride and potassium chlorate in 0.02 molal solution is 0.93 and 0.86, respectively. What are the freezing points of the solutions?

<sup>1</sup> Senter, *Trans. Faraday Soc.*, **15**, 3 (1919).

<sup>2</sup> For a critical review of the theory, see Tutundzhic, *Bull. soc. chim. roy. Yougoslav*, **3**, 109 (1932). According to Tammann, many of the difficulties of the theory are removed if the internal pressure of the solution is considered, *Z. physik. Chem.*, **163A**, 17 (1932).

## CHAPTER IV

### THE PROCESS OF ELECTROLYTIC DISSOCIATION AND CONDUCTANCE

**Atomic and Molecular Structure.** According to the prevailing conception regarding atomic structure, the atom is supposed to consist of a positively charged nucleus surrounded by electrons. The number of these electrons is such that the atom as a whole is electrically neutral. The magnitude of the nuclear charge, and, therefore, the number of planetary electrons, increase with the mass of the atom. In the so-called chemical atom, as distinguished from the atomic model of the physicist, the electrons are assumed to surround the nucleus in successive concentric rings (Kossel), or shells forming a three-dimensional structure (Lewis, Langmuir). The hydrogen nucleus is associated with only one electron. The nucleus of the helium atom is associated with two electrons, both of which are in the same ring or shell. The nuclei of the atoms of Li, Be, B, C, N, O, F, and Ne are associated with two electrons in the inner ring or shell, and with 1, 2, 3, 4, 5, 6, 7, and 8 electrons, respectively, in the second ring or shell. The atoms of the next eight elements in the periodic system, sodium to argon, have two electrons in the first, eight in the second, and successively one to eight electrons in the third ring or shell. This conception of atomic structure gives a satisfactory interpretation of many of the important relationships among the elements.

The electrons are supposed to attain the greatest symmetry and stability in atoms of the inert gases. Other atoms are assumed to have a tendency to attain the structure of the nearest inert gas by taking or giving up electrons. As pointed out above, atoms of neon and argon have eight, and atoms of helium two, electrons in the outer shell or ring. Suppose we bring together two atoms, one of which can attain the inert gas structure by giving up an electron, and the other by gaining an electron. If the exchange occurs, the former will become positively charged (owing to the loss of an electron) and the latter negatively charged (owing to the gain of an electron). As a result of the electrostatic attraction thus created, the two atoms may approach sufficiently close to one another to form a molecule. On this basis the formation of a

molecule of sodium fluoride from its constituents is pictured in Fig. 16. In this figure the dots represent the distribution of the electrons in the outer shell of the fluorine atom and the second and third shells of the sodium atom. Compounds formed in this manner are called

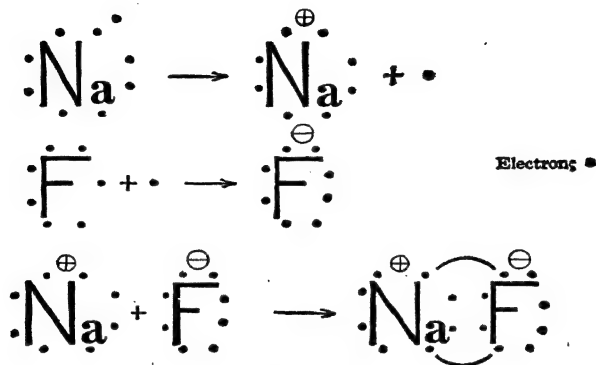
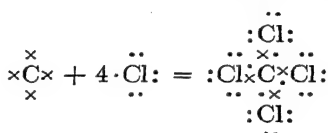


FIG. 16.

electrovalent compounds. Chemical combination may also take place between atoms as the result of the *sharing* of electrons. Thus



where the crosses represent the electrons belonging to the carbon atom and the dots those belonging to the chlorine atoms. Compounds of this type are called covalent compounds. There is good evidence for believing that electrovalent compounds are always ionized, even in the solid state, whereas covalent compounds, in which the constituents are held together by the sharing of electrons, are never ionized. If the electrostatic attractive forces existing in an ionized compound are sufficiently weakened, dissociation of the ions occurs. Compounds are known, however, which are ionized in some states and un-ionized in others.

The electrostatic attractive forces exerted between the oppositely charged ions of an electrovalent compound may be so great as to draw them close enough together to cause electrons associated with one atom to be *shared* with another. Fajans and Joos<sup>1</sup> pointed out that the

<sup>1</sup> *Z. Physik*, **23**, 1 (1924).



change from electrovalency which thus results takes place the more readily: (1) the greater the charge of the ions; (2) the smaller the cation; (3) the larger the anion. Conversely, when the charge on the ions is small or when the cation is large and the anion small, a covalent union will tend to change to an electrovalent one. Thus under favorable conditions an electrolyte may change to a non-electrolyte, or *vice versa*. In view of this it is not surprising that, in beryllium chloride with a small cation having two positive charges, the union between the atoms is largely covalent, as indicated by its very low conductance in the molten state. In group III of the periodic system, it is not until scandium is reached that the molten chloride is a conductor.<sup>1</sup>

**The Dissociating Power of the Solvent.** As we have seen, an electrolyte when dissolved in a solvent dissociates into ions. Without going



FIG. 17.

into the causes or the mechanism of the process of dissociation at present, it may be assumed that the solvent in some way lessens the attractive forces holding the oppositely charged constituents together, thereby rendering them free to move under the influence of an electric field. This conception is depicted in Fig. 17.

Numerous investigations carried out during the first quarter of the century have shown that the capacity for dissociation of a substance varies in different solvents. It is of importance, therefore, to ascertain why some solvents yield solutions which are much better conductors of electricity than others. Although many factors are known which affect the conductance of solutions, the results of Walden's<sup>2</sup> comprehensive measurements of the electrolytic conductance of a single solute, in a large number of widely different solvents, have shown that undoubtedly a *basic relation exists between the dissociation power of a solvent and its dielectric constant and the degree of unsaturation of its simple molecules.*

**The Dielectric Constant and the Dissociating Power of the Solvent.** If  $f_0$  represents the attracting or repelling force of unlike or like charges of electricity when they are separated by a vacuum, then when they are separated by some form of matter the attracting or repelling force,  $f$ , is

<sup>1</sup> Biltz and Klemm, *Z. anorg. Chem.*, **152**, 267 (1926).

<sup>2</sup> *Z. physik. Chem.*, **46**, 103 (1903); **54**, 129 (1906).

equal to  $f_0/\epsilon$ , where for a given kind of matter  $\epsilon$  is a constant—the so-called **dielectric constant**<sup>1</sup> of the medium. The electric field set up by these charges causes the positive and negative charges of the molecules of the separating medium to assume a non-uniform distribution, i.e., to become **polarized**. Since these polarized molecules, or induced dipoles, themselves set up an opposing electric field, the value of  $f_0$  is decreased. If  $e_1$  and  $e_2$  represent electric charges, which are separated by a distance  $l$ , then

$$f = \frac{1}{\epsilon} \cdot \frac{e_1 e_2}{l^2} \quad (1)$$

This relation, which was first verified by Coulomb, is known as *Coulomb's law* or the *law of electrostatic force*. The dielectric constant of air is usually taken as unity, although it is actually slightly greater (1.00058 at room temperature).<sup>2</sup> The values of the dielectric constant of different substances vary considerably (see Table XI). In general, the dielectric constant decreases with rise in temperature. According to Debye,<sup>3</sup> the change is given by the expression:

$$\frac{(\epsilon - 1)}{(\epsilon + 2)} \cdot \frac{1}{T \cdot d} = a + bT \quad (2)$$

where  $d$  is the density of the substance,  $T$  the absolute temperature, and  $a$  and  $b$  are constants. The results of later measurements,<sup>4</sup> however, did not entirely verify this equation.

As mentioned in the preceding chapter, a connection between the dielectric constant of a solvent and its dissociating power was first suggested by J. J. Thomson,<sup>5</sup> in 1893. He put forward the hypothesis that "if the forces which hold the molecule together are electrical in their origin, . . . these forces will be very much diminished when the molecule . . . is surrounded by a substance possessing a very large inductive capacity." On the assumption that chemical forces are electrical in their origin, Nernst<sup>6</sup> pointed out, in the following year, that solvents

<sup>1</sup> For methods of measuring the dielectric constant, see Joachim, *Ann. Physik*, **60**, 570 (1919); King and Patrick, *J. Am. Chem. Soc.*, **43**, 1835 (1921); Hyslop and Carman, *Phys. Rev.*, **15**, 243 (1920); Waibel, *Ann. Physik*, **72**, 161 (1923); Fritts, *Phys. Rev.*, **23**, 345 (1924); Williams and Krchma, *J. Am. Chem. Soc.*, **48**, 1888 (1926); Daniels, Mathews, and Williams, *Experimental Physical Chemistry*, 1941. For a critical review of methods, see Lattey, *Phil. Mag.*, **41**, 829 (1921).

<sup>2</sup> Tanyl, *Ann. Physik*, **23**, 559 (1907); **26**, 59 (1908).

<sup>3</sup> *Physik. Z.*, **13**, 97 (1912).

<sup>4</sup> Jezewski, *J. phys. radium*, **3**, 293 (1922).

<sup>5</sup> *Phil. Mag.*, **36**, 313 (1893).

<sup>6</sup> *Z. physik. Chem.*, **13**, 535 (1894).

having the greatest dielectric constants should exhibit the greatest dissociating powers. The combined statements of Thomson and Nernst are known as the *Thomson-Nernst rule*.

Since the dielectric constant of the solvent determines the magnitude of the electrostatic forces between the ions, a rearrangement in their distribution and the formation of ion pairs will be less extensive in solvents of high dielectric constant. Also, the weakening of these forces by the solvent may be sufficiently great to lessen the tendency for an electrovalency to change to a covalency. Thus beryllium chloride, although a poor conductor in the molten state, conducts electricity readily when dissolved in a solvent with a high dielectric constant like water.

In order to determine the relation between these two properties of solvents, Walden<sup>1</sup> made a systematic study of the dissociating power of almost every type of organic liquid, including representatives of the alcohols, aldehydes, ketones, acids, acid anhydrides, chlorides, bromides, amides, esters, nitriles, thiocyanates, and nitro compounds at 25°. To facilitate the comparison of the dissociating power of the different solvents, one solute—tetraethylammonium iodide—was employed throughout. The results of this investigation are in agreement with the Thomson-Nernst rule, and show clearly the close parallelism between the magnitude of the dielectric constant ( $\epsilon$ ) of the solvent and its dissociating power: *the greater the dielectric constant of the solvent, the greater the apparent percentage dissociation* of tetraethylammonium iodide at a given concentration ( $c$ ). This relation is illustrated by the data in Table XI. The high dissociating power of water agrees with its position in the table, for of all the common solvents it possesses the greatest dielectric constant. Formamide, with a dielectric constant slightly greater than that of water, imitates in a remarkable manner many of the physical characteristics and constants of water. It may be mentioned here that hydrocyanic acid ( $\epsilon = 95$ ) has a dissociating power even higher than that of water.<sup>2</sup> Results similar to those recorded in Table XI were obtained by Creighton and Way<sup>3</sup> with trimethyl-para-tolylammonium iodide and a number of representative solvents. Walden showed<sup>4</sup> that the Thomson-Nernst rule is valid in a quantitative as well as in a qualitative sense for solutions of typical binary salts in a number of solvents of low dielectric constant (2.1–3.76).

<sup>1</sup> *Z. physik. Chem.*, **46**, 103 (1903); **54**, 129 (1906); cf. also Kraus and Fuoss, *J. Am. Chem. Soc.*, **55**, 21, 1019 (1933).

<sup>2</sup> Centnerszwer, *Z. physik. Chem.*, **39**, 217 (1902).

<sup>3</sup> *J. Franklin Inst.*, **186**, 675 (1918); **187**, 313 (1919).

<sup>4</sup> *Z. physik. Chem.*, **147A**, 1 (1930).

TABLE XI

RELATION BETWEEN THE DIELECTRIC CONSTANT AND THE DISSOCIATING POWER  
OF SOLVENTS

(Temperature = 25°)

Solvent	$\epsilon$	Apparent Percentage Dissociation		
		$c = 0.01$	$c = 0.001$	$c = 0.0005$
Water.....	81.7	91	98	99
Formamide.....	84.0	93	98	98
Glycetonitrile.....	67.9	93	98	99
Succinonitrile.....	57.3-61.2	90	95	96
Citraconic anhydride.....	39.5	82	93	94
Nitromethane.....	38.2-40.4	78	92	93
Furfuraldehyde.....	36.5-39.4	ca. 78	91	93
Lactonitrile.....	37.7	..	89	91
Acetonitrile.....	35.8-36.4	74	90	92
Methylthiocyanate.....	33.3-35.9	77	89	91
Ethylene glycol.....	34.5	78	89	..
Nitrobenzene.....	33.4-37.4	71	88	90
Methyl alcohol.....	32.5-37.4	73	88	90
Methylcyanacetate.....	28.8	69	84	87
Propionitrile.....	26.7-27.2	65	84	87
Ethylthiocyanate.....	26.5-31.2	63	83	86
Ethylcyanacetate.....	26.2-26.7	65	83	87
Benzonitrile.....	26.0	61	80	84
Epichlorohydrin.....	26.0	60	81	85
Acetylacetone.....	25.1-26.0	..	83	87
Ethyl alcohol.....	21.7-27.4	54	78	82
Acetone.....	20.7-21.9	50	74	80
Ethyl thiocarbamide.....	19.4-22.0	..	66	..
Acetic anhydride.....	17.9	58	79	84
Benzaldehyde.....	14.5-16.9	51	73	78
Phenylacetoneitrile.....	15.0-16.7	46	74	79
Acetyl bromide.....	16.2	47	73	78
Acetyl chloride.....	15.5	46	72	79
Salicylaldehyde.....	13.9	34	55	61

An interesting empirical relation yielded by Walden's data is expressed by the formula

$$\epsilon \sqrt{\frac{1}{c}} = \text{constant} \quad (3)$$

where  $c$  is the concentration at which the degree of dissociation of tetraethylammonium iodide has a definite value in any solvent.

Since there appears to be little doubt that the dielectric constant is a controlling factor in the process of electrolytic dissociation, the determination of the dielectric constants of solutions of electrolytes has become a matter of considerable importance. By the use of oscillations of short wavelength, measurements have been made <sup>1</sup> of the dielectric constants of solutions of several electrolytes in a number of solvents. It has been found that successive small additions of solute to the solvent cause the dielectric constant to decrease to a minimum and then to rise. The depressing effect of an ion on the dielectric constant of water depends upon the charge and not upon the chemical nature of the ion. Thus ions of the same valence produce the same depressing effects.

**The Dielectric Constant and the Associating Power of the Solvent.** According to Walden,<sup>2</sup> the value of the dielectric constant of a liquid depends largely upon the presence of certain chemical groups. He has found that it is increased by the substitution of the following groups, the magnitude of the increase becoming greater in the order from left to right:

I, Br, Cl, F, NH<sub>2</sub>, CN, CO<sub>2</sub>H, CHO, CO, NO<sub>2</sub>, OH

This is almost the same order in which Auwers <sup>3</sup> found that the substitution of these groups increased the ability of the solvent to prevent association of the molecules of the solute. The influence of these groups upon the dielectric constant and upon the associating power of a solvent indicates that there must be some connection between these two properties. One and the same solute can, according to the nature of the solvent, show all possible degrees of association, and here the dielectric constant plays a determining role: the degree of association is greater the smaller the value of the dielectric constant. Quantitatively, Walden <sup>4</sup> showed that for the same degree of association,  $x_1 = x_2 = x_3 \cdots = \text{constant}$ ,

<sup>1</sup> Walden, Ulich, and Werner, *Z. physik. Chem.*, **110**, 43 (1924); **115**, 177 (1925); **116**, 261 (1925); Hooper and Kraus, *J. Am. Chem. Soc.*, **56**, 2265 (1934); Geddes and Kraus, *Trans. Faraday Soc.*, **32**, 585 (1936).

<sup>2</sup> *Z. physik. Chem.*, **70**, 569 (1910).

<sup>3</sup> *Ibid.*, **42**, 513 (1903).

<sup>4</sup> *Ibid.*, **94**, 295 (1920).

of a given solute in different solvents having dielectric constants,  $\epsilon_1$ ,  $\epsilon_2$ ,  $\epsilon_3$ , ..., the following rule holds:

$$\epsilon_1 \sqrt[3]{\frac{1}{c_1}} = \epsilon_2 \sqrt[3]{\frac{1}{c_2}} = \epsilon_3 \sqrt[3]{\frac{1}{c_3}} = \text{constant} \quad (4)$$

$c_1$ ,  $c_2$ ,  $c_3$ , ... being the concentrations of the solute in the different solvents. For different degrees of association,  $x$ ,

$$x\epsilon \sqrt[3]{\frac{1}{c}} = \text{constant} = 36 \quad (5)$$

A comparison of the values of the mole number which have been obtained for non-aqueous solutions by various methods often leads to contradictory results. Sometimes  $i$  values which are less than unity are obtained by the freezing-point method, even though the conductance method indicates that the solute must be dissociated to a considerable extent in the solution. This anomaly may be explained, however, if we assume that in such cases the number of molecules which dissociates is exceeded by the number which associates. Sometimes the same solvent possesses the power of dissociating certain solutes and associating others. For example, whereas formic acid dissociates potassium chloride, hydrogen chloride apparently exists as double molecules in this solvent.<sup>1</sup>

**Polarity of Molecules.** When atoms combine to form a symmetrical

molecule, such as carbon tetrachloride  $\left( \begin{array}{c} :\ddot{\text{Cl}}: \\ :\ddot{\text{Cl}}:\ddot{\text{C}}:\ddot{\text{Cl}}: \\ :\ddot{\text{Cl}}: \end{array} \right)$ , the mean elec-

trical center (analogous to center of gravity) of the positive nuclei coincides with the corresponding center of all the electrons, and the molecule does not have an electrostatic moment ( $\mu$ ). In unsymmetrical molecules,

such as water ( $\text{H}:\ddot{\text{O}}:\text{H}$ ), ammonia  $\left( \begin{array}{c} :\ddot{\text{N}}: \\ \text{H} \end{array} \right)$ , and sulphur dioxide

$(:\ddot{\text{O}}::\ddot{\text{S}}:\ddot{\text{O}}:)$ , the centers of the opposite charges do not coincide, and each of these molecules may be regarded as a permanent dipole, the electric moment of which is equal to the product of the distance between the two centers and the total electric charge of either sign in the molecule. Thomson<sup>2</sup> called molecules of the latter kind **polar molecules**, and those of the former type, **non-polar molecules**. A few examples of these two types of molecules are given in Table XII. When a liquid the

<sup>1</sup> Zanninovich-Tessarini, *ibid.*, 19, 257 (1896).

<sup>2</sup> *Phil. Mag.*, 27, 757 (1914).

molecules of which are polar is placed in an electric field, this field will tend to orient the electric doublets in such a manner as to reduce their potential energy to a minimum.

TABLE XII  
POLAR AND NON-POLAR MOLECULES

Polar Molecules	Non-Polar Molecules
Water	Carbon bisulphide
Ammonia	Carbon tetrachloride
Hydrocyanic acid	Benzene
Methyl and ethyl alcohols	Nitrous oxide
Hydrogen chloride	Hexane
Formamide	Oxygen

Although the terms "polar" and "non-polar" molecules are suggestive, they are only qualitative terms. It is much better to speak of the polarity of molecules, which can be expressed quantitatively in terms of their electric (dipole) moments. The magnitude of the polarity of molecules (as measured by their electric moments) varies considerably, as is shown by the data<sup>1</sup> in Table XIII. In this table the symmetrical (non-

TABLE XIII  
ELECTRIC MOMENTS OF MOLECULES

Molecules	$\mu \times 10^{18}$ esu	Molecules	$\mu \times 10^{18}$ esu
Carbon tetrachloride *	0.0	<i>o</i> -Chlorophenol	1.43
<i>p</i> -Xylene *	0.0	<i>m</i> -Chlorophenol	2.17
Chloroform	1.10	<i>p</i> -Chlorophenol	2.68
Ethyl ether	1.22	<i>o</i> -Nitrophenol	3.10
Chlorobenzene	1.55	<i>m</i> -Nitrophenol	3.90
Phenol	1.70	<i>p</i> -Nitrophenol	5.05

polar) molecules are indicated with an asterisk. Since molecular dimensions are of the order of  $10^{-8}$  centimeter and the unit of electric charge is  $4.80 \times 10^{-10}$  esu, all electric moments are of the order of  $10^{-18}$  esu. The magnitude of the electric moment of a dissymmetrical molecule varies with temperature; that of a symmetrical molecule does not.

The electric moment of a molecule can be determined by means of the following modification of equation 2:

$$P = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d} = \frac{4\pi N}{3} \left( a + \frac{\mu^2}{3kT} \right) = P_d + P_o \quad (6)$$

<sup>1</sup> Williams and Krehma, *J. Am. Chem. Soc.*, **49**, 1676 (1927); Williams and Fogelberg, *ibid.*, **52**, 1356 (1930).

where  $P$  is the molar polarization,  $N$  is Avogadro's number,  $\mu$  is the electric moment,  $k$  is Boltzmann's constant (i.e., the ratio of the gas constant,  $R = 8.315 \times 10^7$ , to Avogadro's number),  $a$  is a constant, and the other quantities have their usual significance. It is evident that the molar polarization is made up of two parts:

$$P_d = \frac{4\pi}{3} \cdot N a \quad (7)$$

which denotes a polarization due to deformation of the molecule or to its induced dipole; and

$$P_o = \frac{4\pi}{3} \cdot N \cdot \frac{\mu^2}{3kT} \quad (8)$$

which denotes a polarization due to orientation of the molecule in the field, in consequence of its permanent dipole.

The molar polarization of a molecule which has no electric moment is given simply by equation 7, since then  $P = P_d$ . If the molecule has a moment, the value of the  $P_o$  term may be very closely approximated if the  $P_d$  term can be determined, for the total molar polarization,  $P$ , of any substance, in the solid, liquid, or gaseous state, can be calculated if its dielectric constant, density, and molecular weight are known. The electric moment of the molecules of a substance is most readily determined when it is in the gaseous state;<sup>1</sup> in the liquid state its determination is somewhat more difficult.<sup>2</sup>

Two general methods of procedure have been employed to determine the electric moments of the molecules of a liquid. The first, suggested by Errera,<sup>3</sup> is very ingenious and depends upon the assumption that the difference between the molar polarization  $[(\epsilon - 1/\epsilon + 2) \times M/d]$  of the molecules of a substance in the liquid and solid states should be a measure of the dissymmetry and, therefore, of the orientation polarization ( $P_o$ ), the reasoning being that in the solid state there can be no free orientation of the molecules (i.e.,  $P_o = 0$ ). It is doubtful, however, whether the results obtained by this method are very accurate. In the second method,<sup>4</sup> which is probably more accurate, the molecules whose

<sup>1</sup> For methods, see Zahn, *Phys. Rev.*, **24**, 400 (1924); Sanger, *Physik. Z.*, **27**, 556 (1926); Braunmuhl, *ibid.*, **28**, 597 (1927).

<sup>2</sup> Debye, *Physik. Z.*, **13**, 97 (1912); *Verh. deut. physik. Ges.*, **15**, 777 (1913); *Handb. d. Radiologie*, **6**, 625 (1925); Lange, *Z. Physik*, **33**, 169 (1925); Smyth, *J. Am. Chem. Soc.*, **49**, 1030 (1927); Williams and Krehma, *ibid.*, **49**, 1676 (1927).

<sup>3</sup> *J. Phys. Radium*, **6**, 390 (1925); *Physik. Z.*, **27**, 764 (1926). The latter is replete with references to his earlier work.

<sup>4</sup> Debye, *Physik. Z.*, **13**, 97 (1912); *Verh. deut. physik. Ges.*, **15**, 777 (1913).



electric moment is to be determined are dissolved in a non-polar solvent and the dielectric constant, the density, and the refractive index ( $n$ ) of the solution measured.<sup>1</sup>

The molar polarization ( $P_{1,2}$ ) of a binary mixture is given by the expression:

$$P_{1,2} = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{N_1 M_1 + N_2 M_2}{d_{1,2}} = N_1 P_1 + N_2 P_2 \quad (9)$$

where  $N_1$  and  $N_2$  are the mole fractions, and  $P_1$  and  $P_2$  are the molar polarizations of the solvent and solute, respectively. If it is assumed that  $P_1$  is proportional to  $N_1$  at all concentrations,<sup>2</sup> the term  $P_2$  may be calculated readily. Then, since the molar polarization due to deformation ( $P_{2d}$ ) is equal to the molar refractivity of the pure solute, as calculated by the Lorenz and Lorentz formula, i.e.,

$$P_{2d} = \frac{n_2^2 - 1}{n_2^2 + 2} \cdot \frac{M_2}{d_2} \quad (10)$$

and since

$$P_2 = P_{2d} + P_{2o} \quad (11)$$

it follows that

$$P_{2o} = P_2 - P_{2d} = \frac{4\pi}{3} \cdot N \cdot \frac{\mu_2^2}{3kT} \quad (12)$$

Hence

$$\mu_2 = \sqrt{\frac{(P_2 - P_{2d}) \times 9kT}{4\pi N}} \quad (13)$$

**Unsaturation of the Molecules and the Degree of Association of the Solvent.** Polar molecules are unsaturated, unsaturation resulting from the presence of electrons which are free to move under the influence of an electric field. For example, a water molecule has at least two electrical doublets,  $H^+ \rightarrow -O^- \leftarrow H^+$ , in which the six outer electrons of the oxygen atom can assume such a position as to exert a maximum attraction on the positive portion of the doublet, and in this way give rise to an unequal distribution of the electric charges. When two polar molecules are close together, the unequal distribution of the charges is more pronounced, and the mutual attraction may be sufficient to bring about combination or *association* of the simple molecules. Since the polymerized molecule has a greater electrostatic moment than the simple molecule, the constraints on the electrons are accordingly weaker and

<sup>1</sup> The effect of the solvent in the measurement of dipole moments is discussed by Glasstone, *Chem. Soc., Ann. Repts.*, 1936, 117-34.

<sup>2</sup> The right to make this assumption is questionable.

the attractive forces exerted on neighboring molecules correspondingly greater. Consequently, a still more complex molecule may result. *The higher the degree of association of a solvent, the larger the electrostatic moment of its molecules and the weaker the forces holding the electric charges, that is, the higher the dielectric constant of the solvent.*<sup>1</sup> The reverse is not true, however, for many liquids with high dielectric constants are not associated. The parallelism existing between the degree of association and the dielectric constant of solvents is shown by the data in Table XIV.<sup>2</sup>

TABLE XIV

SUBSTANCE	DEGREE OF ASSOCIATION	DIELECTRIC CONSTANT
Formamide	6.18	84
Water	3.81	81.7
Formic acid	3.61	58
Acetic acid	3.62	6.3
Methyl alcohol	3.42	32.5
Glycol	2.92	34.5
Ethyl alcohol	2.74	21.7-27.4
Acetonitrile	1.67	36
Propionitrile	1.45	26.8
Acetone	1.26	21.3
Benzonitrile	0.97	26.0
Nitrobenzene	0.93	35

The influence of the unsaturation of a solvent on its dissociating power is seen clearly in solutions of silver nitrate in benzonitrile and propionitrile. According to Schlundt,<sup>3</sup> the dissociation of this solute is markedly greater in the latter than in the former solvent. Although the dielectric constants of these solvents are almost equal, it will be observed, from the values given in Table XIV, that although the molecules of benzonitrile do not associate, those of propionitrile polymerize to a considerable extent.

**Mechanism of the Process of Electrolytic Dissociation.** Although it is evident that the dielectric constant of the solvent, which determines the magnitude of the electrostatic forces between the ions, is a controlling factor in the process of electrolytic dissociation, it is not the only one. On the basis of several years' experimental work on addition compound formation,<sup>4</sup> which showed that conducting solutions invariably afforded evidence of the formation of complexes between the solute and solvent,

<sup>1</sup> Cf. Kendall, *J. Am. Chem. Soc.*, **39**, 2323 (1917).

<sup>2</sup> Walden, *Z. physik. Chem.*, **54**, 129 (1906).

<sup>3</sup> *J. Phys. Chem.*, **5**, 168 (1901).

<sup>4</sup> Kendall, Booge, and Andrews, *J. Am. Chem. Soc.*, **39**, 2303 (1917).

Kendall and Booge<sup>1</sup> reached the conclusion that electrolytic dissociation "is preceded by combination between solute and solvent and is, indeed, a consequence of such combination." Evidence of the formation of a definite compound of solute and solvent is incomplete, but it is probable that an important factor in electrolytic dissociation is the power of the solvent to accept electrons from or to donate them to the ions of the solute, thereby establishing a co-ordinate union between ion and solvent molecule. As Hartley<sup>2</sup> points out, "it is significant that, in non-hydroxylic solvents such as nitromethane, which can only form a coordinate link with the cation, most lithium salts are weak, in spite of the high dipole moment of the solvent molecules, indicating the importance of a chemical link between the anion and the solvent in preventing ionic association."

We have seen in the preceding section that the simple unsaturated molecules of the solvent may combine to form complex molecules, owing to the attractive forces resulting from an unequal distribution of the electrical charges of the simple molecules; and that this inequality of distribution is more pronounced, and therefore the electrical forces greater, in the complex than in the simple molecules. Accordingly, we should expect, when an electrovalent compound is placed in a solvent consisting of polar molecules, that the associated molecules of the solvent would exert, on the ions of the compound, attractive forces, which would be greater the higher the degree of unsaturation of the solute, or the stronger the fields of electric force furnished by them. In this way the attractive forces between the ions of the solute would be diminished, and they would pass into solution surrounded by solvent molecules.

Ions formed in this manner are not simple charged atoms or groups, but combinations of these with molecules of the solvent. In addition to bringing about the dissociation of the solute, the solvent molecules tend to keep the dissociated portions apart by enveloping them in an oppositely charged layer and, in this way, weakening their mutual attraction. Thus, in an aqueous solution of copper chloride, the positively electrified copper atom would be adjacent to the negative ends of polar water molecules, and as a result its attraction for negative chlorine ions would be decreased.<sup>3</sup>

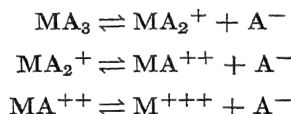
<sup>1</sup> *J. Am. Chem. Soc.*, **39**, 2323 (1917); cf. also Kendall, *Proc. Natl. Acad. Sci. U.S.*, **7**, 56 (1921); Thomson, *J. Franklin Inst.*, **195**, 734 (1923).

<sup>2</sup> *Chem. Soc., Ann. Repts.*, **27**, 353 (1930).

<sup>3</sup> A comprehensive list of references on this subject is given by Fricke, *Z. Elektrochem.*, **28**, 161 (1922). See also Remy, *Z. physik. Chem.*, **118**, 161 (1925); *Trans. Faraday Soc.*, **23**, 381 (1927); Taylor and Sawyer, *J. Chem. Soc.*, **1929**, 2095; Butler and Connell, *Nature*, **131**, 800 (1933).

In summarizing the evidence it appears, therefore, that the influence of the solvent on electrolytic dissociation depends (1) upon the magnitude of its dielectric constant, which determines the force of attraction between the ions and the energy required to separate them; and (2) upon the extent to which it associates with the ions as a consequence of its dipole character or the formation of co-ordinate linkages, thus decreasing the tendency to form ion pairs or undissociated molecules. This power of the solvent to prevent the formation of ion pairs seems to depend less on the magnitude of its electric moment than on its ability to form co-ordinate linkages with both ions.

The hypothesis has been advanced by Harkins and Pearce<sup>1</sup> that all electrolytes which form more than two ions undergo a stepwise dissociation, and yield intermediate ions which are present in dilute as well as in concentrated solutions. In a quaternary electrolyte,  $MA_3$ , for example, dissociation may be represented by the scheme:



Thus a ternary electrolyte, such as potassium sulphate, is capable of giving one intermediary ion, and a quaternary electrolyte, such as lanthanum nitrate, is capable of giving two intermediate ions. The

TABLE XV  
DISSOCIATION OF TERNARY ELECTROLYTES

Equivalent Concentration of Salt	Silver Sulphate			Potassium Sulphate		
	Percentage of Sulphate as:					
	Ag <sub>2</sub> SO <sub>4</sub>	AgSO <sub>4</sub> <sup>-</sup>	SO <sub>4</sub> <sup>--</sup>	K <sub>2</sub> SO <sub>4</sub>	KSO <sub>4</sub> <sup>-</sup>	SO <sub>4</sub> <sup>--</sup>
1.0	....	....	....	12.0	46.0	42.0
0.1	7.94	43.7	48.3	5.0	35.2	59.8
0.05	5.97	37.5	56.5	....	....	....
0.01	1.54	21.4	77.0	1.0	18.0	81.0

<sup>1</sup> *J. Am. Chem. Soc.*, **38**, 2679 (1916); cf. Drucker, *et al.*, *Z. Elektrochem.*, **19**, 797 (1913).

percentage of the electrolyte present in the form of intermediate ions decreases with the concentration; see Table XV. According to Koch,<sup>1</sup> electrolytic dissociations may be grouped in four categories: (1)  $MA = M^+ + A^-$ , simple symmetrical dissociation; (2)  $3MA = (MAM)^+ + (AMA)^-$ , complex symmetrical dissociation; (3)  $2AM = M^+ + (AMA)^-$ , A unsymmetrical dissociation; (4)  $2MA = (MAM)^+ + A^-$ , M unsymmetrical dissociation. Type 1 occurs in dilute, type 2 in concentrated, solutions. Types 2 to 4, called autocomplex dissociations, depend on the stability of the complex ion; in solvents of a given dipole moment such dissociation depends on the geometrical arrangement of the charge producing the moment.

**The Mechanism of the Transportation of Electricity in Metallic Conductors.** Notwithstanding that the daily transport of electricity through metallic conductors is enormously greater, our knowledge regarding the manner of the passage of electricity through electrolytic conductors is on a much firmer foundation. With the development of our understanding of the structure of matter, an electron theory of metallic conduction was formulated which, in spite of many serious objections raised against it, is still regarded as giving the best interpretation of many facts.

According to the most generally accepted form of the theory, the atoms of metals are supposed to separate continuously into an electron and a positively charged residue. These electrons move about at high velocities in all directions in the interior of the metal. When an electromotive force is applied to the ends of a wire, for example, it is assumed that there is superimposed upon the haphazard motions of the electrons, which result from thermal agitations, a steady flow or drift of electrons along the wire. This flow constitutes the electric current, which is thus conveyed solely by electrons. The rise in temperature which is invariably associated with the transport of electricity through a metal is ascribed to collision of these electrons with the atoms of the metal. Although it might be supposed that the positively charged residues would also move through the metal under the influence of the electric field, for many years careful experiments failed to detect such a movement. Later, however, several investigators observed the movement of ponderable matter during the passage of electricity through metallic conductors. For example, when a current is passed through a glowing wire of palladium-gold alloy the palladium accumulates at the cathode end.<sup>2</sup> Similar behavior has been noted with a gold-lead alloy<sup>3</sup> at 150-

<sup>1</sup> *Phil. Mag.*, **11**, 1122 (1931).

<sup>2</sup> Jost and Linke, *Z. physik. Chem.*, B, **29**, 127 (1935); cf. Schwarz and Stockert, *Z. Elektrochem.*, **45**, 464 (1939).

<sup>3</sup> Seith and Etzold, *Z. Elektrochem.*, **40**, 829 (1934).

180° C, and with steel wires <sup>1</sup> at about 1000° C carbon migrates to the cathode.

Direct evidence in support of the free electron theory of metallic conductance is very meager. From the results of measurements on the current flow produced in metals when accelerated, Tolman and Stewart <sup>2</sup> concluded that the process is of the nature of a drift of electrons. Richardson <sup>3</sup> adduced a number of arguments in support of the same conclusion. On the other hand, the results of measurements of the conductance of alkali amalgams <sup>4</sup> indicated that the mechanism of the transport of electricity in this type of metallic conductor is a more complicated phenomenon than a mere drift of electrons. The following values, multiplied by  $10^{17}$ , have been obtained <sup>5</sup> for the concentration per cubic centimeter of free electrons at 0° C: Na = 1, Bi = 1, Pb = 1.1, Ag = 1.4, Pt = 1.5, Cu = 1.7.

The free electron theory of metallic conduction apparently encountered insuperable difficulties in the "super conductance" of metals, discovered by Onnes, <sup>6</sup> at about 4° K, at which temperature the conductance becomes about  $10^{11}$  times that at 0° C, for, as Thomson <sup>7</sup> pointed out, no permissible increase in the number of free electrons or in their mean free path would explain this enormous increase in the conductance. Accordingly, the free electron theory was abandoned by Thomson, who put forward <sup>7,8</sup> a modification of a theory suggested by him in 1881. This new hypothesis, which was shown <sup>9</sup> to meet the difficulties imposed by "superconductance," may be outlined briefly as follows:

The atoms of a metallic conductor are supposed to be electrical doublets which are arranged in a haphazard fashion. When an electromotive force is applied to the ends of the conductor, a certain fraction of the doublets, which is greater the lower the temperature, arrange themselves in a chain under the influence of the electric field, the others pointing in all directions. The doublets in the atoms produce intense electric forces in their neighbor-

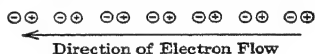


FIG. 18.

<sup>1</sup> Seith and Kubaschewski, *ibid.*, **41**, 551 (1935).

<sup>2</sup> *Phys. Rev.*, **8**, 97 (1916); **9**, 164 (1917).

<sup>3</sup> *Electron Theory of Matter*, p. 408, 1916.

<sup>4</sup> Lewis, G. N., Adams, and Lanman, *J. Am. Chem. Soc.*, **37**, 2656 (1915); Hine, *ibid.*, **39**, 822 (1917). The electronic properties of conductors have been critically surveyed by Fowler, *Proc. Roy. Soc.*, **A141**, 56 (1933).

<sup>5</sup> Waterman, *Phys. Rev.*, **24**, 366 (1924).

<sup>6</sup> *Inst. intern. phys. Solvay, 4th Conseil*, 1924, 251-301 (1927).

<sup>7</sup> *Phil. Mag.*, **30**, 192 (1915).

<sup>8</sup> *Electrician*, **75**, 274 (1915).

<sup>9</sup> Bialobjeski, *Phil. Mag.*, **45**, 161 (1923).

hoods, which tend to drag electrons out of one atom into another. In this manner, the electrons pass along the line of doublets (Fig. 18).

In both the preceding theories, it is conceded that the electric current is due to the motion of negative electricity—the electrons. The actual flow of electricity in metallic conductors, therefore, is *opposite* to “the direction of the current,” as defined in Chapter I.

**The Mechanism of Conductance in Electrolytic Conductors.** When a sufficiently large electromotive force is applied to two electrodes immersed in a solution of an electrolyte—say, a uni-univalent salt, MA—

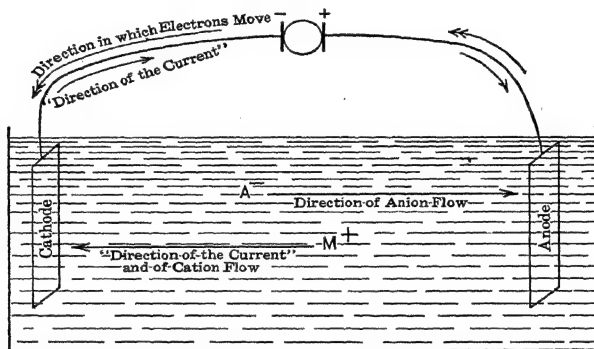
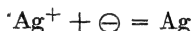


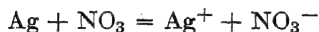
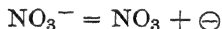
FIG. 19.

all the ions present instantaneously start to move: the cations toward the cathode, and the anions toward the anode. This movement of ions constitutes the flow of electricity through the electrolytic conductor. The direction in which the positive ions travel is arbitrarily taken as “the direction of the current” through the solution. When the source of the electromotive force is a dynamo, electrons flow from its negative side, along the connecting wire, to the cathode. These electrons are acquired by the  $M^+$  ions which become neutral atoms at the cathode. Simultaneously,  $A^-$  ions are discharged by giving up an electron to the anode. These electrons then return along the connecting wire to the positive side of the dynamo. In this way a continuous flow of electrons is maintained from the negative to the positive side of the dynamo (or any other source), as is indicated diagrammatically in Fig. 19. As we have seen in the previous chapter, this exchange of electrons constitutes an electrochemical reaction. The reactions which take place when a solution of copper chloride is electrolyzed between platinum electrodes have already been represented (p. 39). Let us now consider a few other types of electrochemical reactions.

When a solution of silver nitrate is electrolyzed between silver electrodes, the silver ions each take up an electron from the cathode, and deposit on this electrode as neutral atoms:



At the anode, silver enters the solution in the form of ions. The electrochemical changes which take place at this electrode may be represented thus:

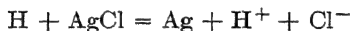
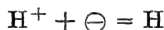


or, simply,

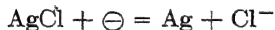


i.e., the neutral silver atoms of the electrode each give up an electron to the anode and enter solution with a single positive charge—as ions. The net result in this electrolysis is the discharge of 1 gram ion of silver at the cathode, and the formation of an equivalent quantity of this ion at the anode, for every faraday of electricity which passes through the solution.

When a solution of hydrochloric acid is electrolyzed between a metal cathode covered with silver chloride, and a silver anode, metallic silver is formed at the cathode and chlorine ions enter the solution:



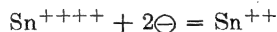
or, simply,



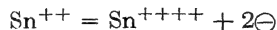
At the anode, silver chloride is produced:



When a solution containing both stannic chloride ( $\text{Sn}^{++++} + 4\text{Cl}^-$ ) and stannous chloride ( $\text{Sn}^{++} + 2\text{Cl}^-$ ) is electrolyzed between platinum electrodes, the electrons coming from the negative side of the source of current convert the stannic ions to stannous ions at the cathode:



while at the anode the stannous ions give up two electrons each and thereby become stannic ions:





The experimental study of the mechanism of the transport of electricity through *solid electrolytic conductors* did not for a long time give very definite results. The difficulties incident to such investigation were, however, successfully overcome by Tubandt and his associates, who obtained positive information relative to the nature of the process of conduction. It was shown<sup>1</sup> that, in the halides of silver, the fluoride and chloride of lead, and silver and cuprous sulphides above their transition points, the process of conductance is analogous to that in solutions. In the lead compounds, the current is carried exclusively by negative ions; in the other substances, by positive ions. In the few solid electrolytes studied, the ion which carries the smaller charge is the one that moves; when both ions have the same charge, the diameter of the ions appears to be the determining factor. Generally under the latter condition it is the cation which moves.<sup>2</sup>

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#### PROBLEMS

1. Measurements which have been carried out with ethyl ether-benzene mixtures at 25° have given for the molar polarization of the ethyl ether the value 54.50. Given that the refractive index and the density of ethyl ether at this temperature are 1.35262 and 0.7077, respectively, calculate the electric moment of the ether molecules.
2. Write the electrochemical equations expressing the electrical and chemical changes which take place when 2 faradays of electricity are passed through: (1) a solution containing ferrous and ferric sulphates, between platinum electrodes; (2) a dilute solution of sulphuric acid, between (a) platinum electrodes and (b) a platinum anode and a cathode of lead dioxide.
3. The mole number of potassium sulphate in 0.005 formal solution is 2.86. Calculate approximately the equivalent concentration of each of the ions present in the solution, assuming that no undissociated molecules of potassium sulphate are present.

<sup>1</sup> Z. anorg. Chem., **110**, 196 (1920); **115**, 105 (1921).

<sup>2</sup> Cf. Friederich, Z. Elektrochem., **32**, 576 (1926).

## CHAPTER V

### ELECTROLYTIC CONDUCTANCE OF SOLUTIONS

**Electrolytic Conductance.** Since the transport of electricity through a solution depends upon the presence of ions, other things being equal, the solution that contains the greatest concentration of ions must be the best conductor. From a study of electrolytic conductance, information may be obtained regarding modifications in the distribution of the ions, leading to the formation of ion pairs or to the establishment of a covalent union between them. On account of the importance of conductance measurements, we shall now consider how they are carried out.

The **specific resistance** of a conductor is defined as the resistance in ohms of a cube of the material 1 centimeter long and 1 square centimeter in cross section. The reciprocal of this quantity is called the **specific conductance** ( $\kappa$ ) of the conductor. When a cube of material of the above dimensions has a resistance of 1 ohm, its specific conductance is unity. The specific conductance of a solution is equal to the reciprocal of its resistance measured between electrodes 1 square centimeter in cross section and 1 centimeter apart. It is expressed in "reciprocal ohms" (mhos). Evidently the specific conductance of a solution is equal to the strength of the current which flows when the solution is placed between electrodes of the aforesaid dimensions between which there is a potential difference of 1 volt, i.e.,

$$I = \frac{E}{R} = \frac{1}{R} = \kappa \quad (1)$$

Since the specific conductance of a solution depends only on the ions of the solute and not on the whole of the material between the electrodes, it must vary with the concentration of the solute. Any variation in the capacity of the solute molecule for conducting electricity, which takes place with change in concentration, cannot be directly determined, therefore, from a study of the specific conductance. Any such variation may be ascertained, however, if we employ parallel electrodes which are kept at a fixed distance of 1 centimeter apart (by suitable insulating material), and which have an area such that that volume of solution which contains 1 mole or equivalent of solute is contained between them.

The conductance which is measured with electrodes of these dimensions is called the **molal conductance** ( $\mu$ ) or the **equivalent conductance** ( $\Lambda$ ). In practice it is not necessary to resort to such cumbersome electrodes, since a simple relation exists between the molar, or equivalent, conductance and the specific conductance. This relation may be obtained

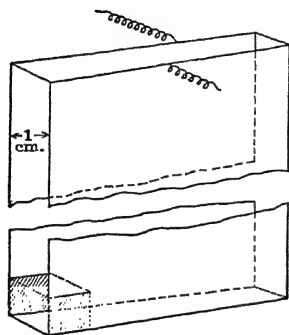


FIG. 20.

from the following consideration: Fig. 20 represents two electrodes which are separated by a distance of 1 centimeter, and which are of such an area that a solution having a volume of  $\phi$  cubic centimeters and containing one equivalent of solute can be contained between them. The shaded portions of the electrodes represent areas 1 centimeter square. Since the conductance of that portion of the solution contained between these shaded areas is, by definition, the specific conductance of the solution, and since each electrode contains  $\phi$  such areas, it follows

that the equivalent conductance of the solution is equal to the product of its specific conductance and the number of cubic centimeters which contains one equivalent of solute. Accordingly, we may write:

$$\Lambda = \phi \kappa \quad (2)$$

Similarly,

$$\mu = \phi \kappa \quad (2a)$$

where  $\phi$  is the number of cubic centimeters of solution which contains 1 mole of solute. Very important information concerning the capacity of the molecules of different dissolved substances for conducting electricity has been obtained from a study of the chemically comparable quantities,  $\Lambda$  and  $\mu$ .

**Conductance Methods.** (a) *Kohlrausch's Alternating-Current Bridge Method.* Of the different means that have been suggested for the measurement of the conductance of solutions, Kohlrausch's alternating-current bridge method is most widely used. Its general adoption has been facilitated by the fact that fairly accurate results can be obtained with simple apparatus of a readily accessible kind. A simple arrangement of the apparatus is shown diagrammatically in Fig. 21. In this figure  $ab$  represents the bridge wire,  $I$  an induction coil or other source of high-frequency alternating current,  $T$  a telephone,  $R$  a variable resistance, and  $K$  a variable air condenser for balancing the capacity of the conductance cell,  $C$ , containing the solution.

When the current from  $I$  reaches the point  $a$ , it divides and travels to  $b$  by the paths  $aRdCb$  and  $acb$ . If the resistance of the solution is equal to that of  $R$ , there will be the same fall of potential from  $a$  to  $d$  as there is from  $a$  to the middle point,  $c$ , of the uniform bridge wire,  $ab$ . Hence, since the points  $c$  and  $d$  are at the same potential, on connecting these points through  $T$  no sound will be heard in the telephone. If, however, the point of contact of the telephone with the bridge wire is moved from

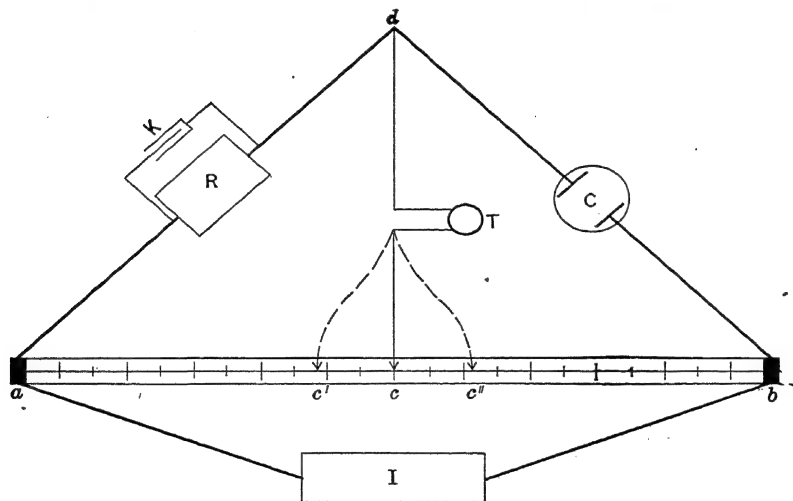


FIG. 21.

$c$  to either  $c'$  or  $c''$ , a current will flow through the telephone and a sound will be heard, owing to the potential difference existing between  $d$  and  $c'$  or  $c''$ . Whatever the resistances of  $R$  and  $C$ , there is some point,  $c$ , on the bridge wire which has the same potential as  $d$ . This point may be obtained by moving the sliding contact along the bridge wire until there is silence in the telephone. This point having been located, the resistance of the solution in  $C$  is given by the expression:

$$R : C = ac : cb$$

or

$$C = R \frac{cb}{ac} \quad (3)$$

It should be mentioned here that in practice it is found better to interchange the source of high-frequency alternating current and the telephone.

Although theoretically there should be silence in the telephone when the points *c* and *d* are at the same potential, it is seldom that a position of silence is obtained in actual practice. Instead of striving to obtain such a position on the bridge wire, the position of *minimum sound* is sought. This may be obtained by taking the mean value of two points on either side of the minimum, at which the sound has the same intensity.

Where a high degree of accuracy is not required, the telephone in Fig. 21 may be replaced by an alternating-current galvanometer. The suitability of this instrument for the determination of electrolytic conductances was investigated by Aten,<sup>1</sup> who found that with sufficiently high resistances and platinized electrodes of adequate surface an accuracy of 0.3 per cent can be readily obtained. This instrument is sufficiently accurate, therefore, for many technical purposes.

Although for many purposes the degree of accuracy attainable by the method just outlined is amply sufficient, the results of several painstaking investigations<sup>2</sup> show that the conductance of solutions may be determined with an accuracy far exceeding that which is generally obtained. These investigations cover a study of the influence of the different factors which affect the measurement of conductance, and include the arrangement of the bridge system, the action of the mechanism for producing alternating currents, the design and construction of the conductance cell, and the proper and efficient use of electromagnetic shielding.

(b) *The Wheatstone Bridge.* A simple form of Wheatstone bridge may be constructed by connecting a so-called slide wire, *ab*, Fig. 21, with the other elements shown in this circuit. A compact and convenient instrument for student work is the circular slide wire shown in Fig. 22. In this the wire is wound in a tight helix mounted on the periphery of a disk which is rotated by a knob on the top. The position of minimum sound is read with an accuracy of 0.1 per cent on a scale observed through an opening in the top of the box containing the instrument. A form of slide wire suitable for more accurate work is shown in Fig. 23. In this the wire is nearly 5 meters long and is wound in a helix of ten turns on a drum. The sliding contact is housed inside the cover of the drum and is moved along the wire by rotating the cover. The number of turns is indicated on a glass scale mounted in front of the cover, while a circular scale engraved on the lower portion of the rotating cover indicates the

<sup>1</sup> *Chem. Weekblad*, **18**, 51 (1922).

<sup>2</sup> Morgan and Lammert, *J. Am. Chem. Soc.*, **48**, 1220 (1926) [this paper gives an excellent summary of earlier work]; Randall and Scott, *ibid.*, **49**, 636 (1927); G. Jones and co-workers, *ibid.*, **50**, 1049 (1928); **51**, 2407 (1929); **53**, 411, 1207 (1931); **55**, 1780 (1933); Shedlovsky, *ibid.*, **52**, 1806 (1930); **54**, 1411 (1932); **56**, 1066 (1934); Luder, *ibid.*, **62**, 89 (1940).

position of a single turn, corresponding to the position of contact. Since the error in reading near the ends of the slide wire produces a greater change in the ratio  $cb/ac$  than an error in reading near the center, the



FIG. 22.

variable resistance should be such that the position of minimum sound lies near the center of the wire.

An inexpensive, flexible student conductance bridge assembly, having an accuracy of measurement of 0.1 per cent or better, has recently been designed and described.<sup>1</sup>

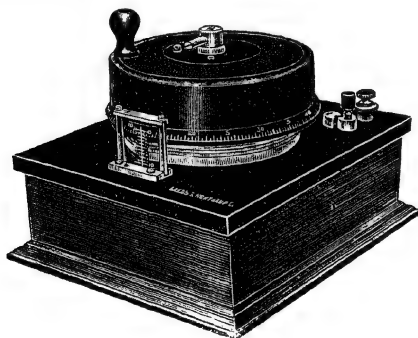


FIG. 23.

A very careful and extensive experimental and theoretical study of the principles and design of the Wheatstone bridge was made by Jones and Josephs.<sup>2</sup> The results obtained in this study led these investigators to

<sup>1</sup> Luder and Vernon, *J. Chem. Education*, **17**, 229 (1940).

<sup>2</sup> *J. Am. Chem. Soc.*, **50**, 1049 (1928); cf. also Luder, *ibid.*, **62**, 89 (1940). These papers should be read by all interested in precision conductance measurements.

design and construct a new form of bridge which has the following improvements over those commonly used:

- a. It has a new and correct method of grounding.
- b. Non-reactive ratio arms are easily adjustable to exact equality of resistance.
- c. Fine adjustment of the resistance down to 0.001 ohm is in the resistance arm instead of the ratio arms.
- d. The reactance balance is significant.
- e. The bridge is sensitive to one part in a million.
- f. It can be used with either direct or alternating current.
- g. It is direct reading.

This bridge <sup>1</sup> (Fig. 24) consists of a box 5 inches deep and 13 by 17 inches in cross section, with a hard rubber top which supports all the electrical parts. The coils, switch contacts, sliding contacts (with one exception), and ground condenser,  $C_g$ , are inside the box. The resistance box,  $R_1$ , is a separate unit and is connected to the bridge by heavy links dipping into mercury cups; the variable condenser,  $C_1$ , is also a separate unit and is shunted across the box. The oscillator, amplifier, and telephone are separate units which are connected at suitable binding posts. The wiring beneath the box is shown in dotted lines. Along one edge are located the binding posts for the ground connection and for the alternating-current or direct-current power lines, and a switch,  $S_3$ , to select one or the other; near at hand is the reversing switch,  $S_4$ . The variable air condenser,  $C_g$ , having a capacitance of 500 micro-microfarads, is mounted with the dial and scale on top and plates inside the box. One side of this condenser is permanently connected to the binding post, which in turn is grounded; its other side may be connected to either of the two alternating-current lines as may be desired by means of the switch,  $S_1$ . From the reversing switch,  $S_4$ , the current passes to the resistance part of the grounding device which is shunted across the line as shown. Resistances  $R_5$  and  $R_6$  are each a 1000-ohm coil of the Ayrton winding. Between  $R_5$  and  $R_6$  is a manganin wire of about 0.75-ohm resistance wound in a single turn around a hard rubber cylinder (placed in one corner of the box for convenience) with a sliding contact,  $g$ , which is always connected to ground. This slider is mounted inside the box, but is controlled by a dial on top. This arrangement makes possible a variation of 0.15 per cent in the ratio of  $R_5$  to  $R_6$ .

One of the novel features of the bridge is the method of grounding, which maintains the telephone when in balance at earth potential, with-

<sup>1</sup> The following description of the bridge follows very closely that given by Jones and Josephs.

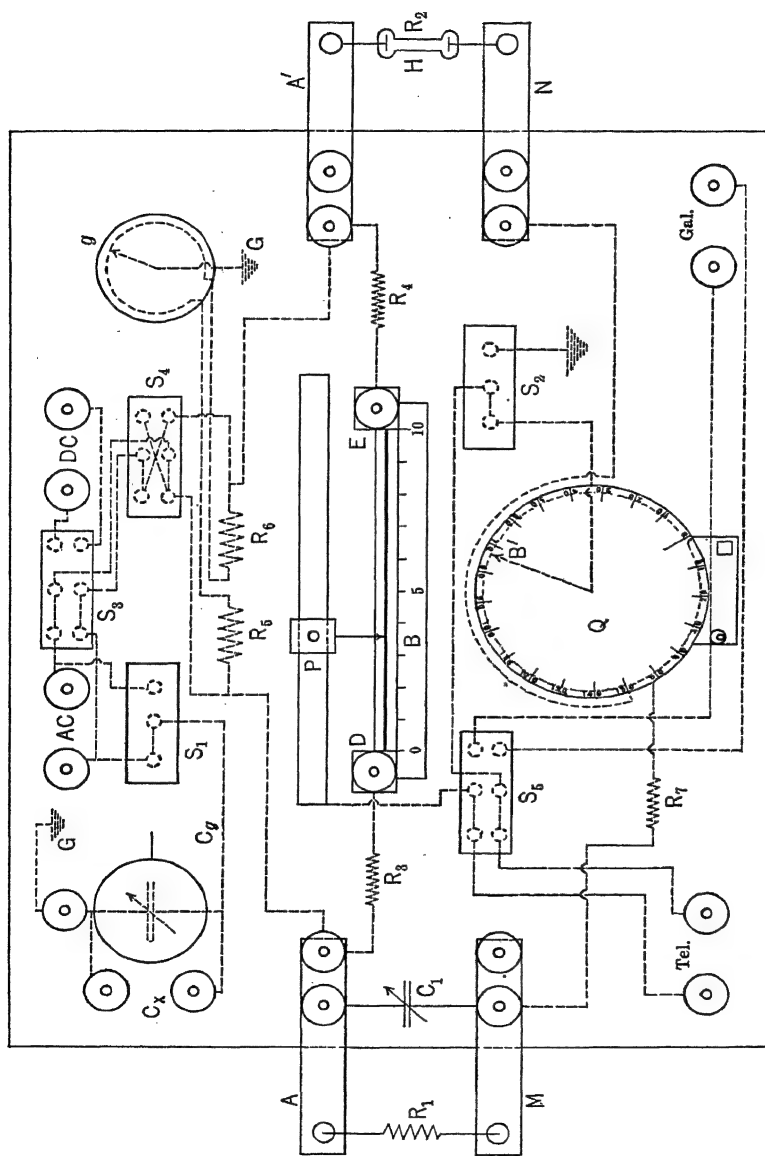


FIG. 24.



out making a direct connection between the bridge and earth as is customarily done. The adjustment of the ground balance, which should be made with every measurement, is carried out as follows: (1) An approximate adjustment of the bridge proper ( $R_1$  and  $C_1$ ) is made, leaving the ground as it happens to be from the last use. (2) By means of the switch,  $S_2$ , the telephone is disconnected from  $B'$  and connected to earth, while the other side of the telephone remains connected to  $B$ . (3) By adjusting the sliding contact,  $g$ , and the variable condenser,  $C_g$ , until there is silence in the telephone,  $B$  is brought to earth potential. (4) The telephone is restored to its original position and its connection with earth broken by means of switch  $S_2$ . (5) The bridge ( $R_1$  and  $C_1$ ) is again adjusted, and, if this second adjustment differs from the original, the adjustment of the ground should be repeated and then the final bridge reading confirmed. The inside of the third of the box containing the resistances  $R_5$  and  $R_6$  is lined with a sheet of copper and grounded. The bridge proper is not shielded.

From the end of the shunt,  $R_5$  and  $R_6$ , the power lines pass through a hole in the shield to the end of the bridge proper,  $A$  and  $A'$ , which consist of heavy nickel-plated brass bars, mounted on top of the box and provided with a mercury cup and two binding posts each.

Between  $A$  and  $A'$  are mounted the ratio arms,  $AB$  and  $BA'$ , consisting of two coils,  $R_3$  and  $R_4$ , each of 1000 ohms of the Ayrton winding. In order that the ratio arms may be adjusted to exact equality, 15 centimeters of a heavy (2 ohms per meter) manganin wire,  $DBE$ , with sliding contact,  $B$ , are mounted between them. With this arrangement a movement of the slider of 1 millimeter changes the ratio of the arms by four parts in a million. The resistance in the sliding contact is not in the bridge circuit proper, but only in the line to the telephone (or galvanometer). Below  $A$  and  $A'$  are two similar bars,  $M$  and  $N$ . The conductance cell,  $H$ , is mounted in the thermostat and connected with suitable lead lines across  $A'$  and  $N$ . The variable resistance box,  $R_1$ , is connected across  $A$  and  $M$  by means of heavy links dipping into mercury cups. A variable condenser,  $C_1$ , of suitable capacitance for the measurements being made is also connected across  $A$  and  $M$ .

The resistance box,  $R_1$ , can be adjusted to tenths of an ohm. Although it is usually preferable to make measurements with 10,000 ohms or more in the cell (i.e., to use cells of a high cell constant—see p. 85), when a box adjustable to tenths of an ohm gives adequate precision, it may sometimes be desirable or necessary to measure resistances as low as 100 ohms. In such cases there is required a means of adjusting the resistance continuously with a means for measuring in thousandths of an ohm. This is accomplished through a single turn of manganin wire mounted on the

cylinder,  $Q$ , with sliding contact,  $B'$ , which is the midpoint of the bridge. An auxiliary resistance,  $R_7$ , of the proper magnitude to bring the midpoint of the resistance between  $M$  and  $N$  at the point marked zero on the dial, is inserted between  $M$  and the slide wire. Then if the slider,  $B'$ , is at zero, the resistance between  $M$  and  $B'$  is equal to the resistance between  $N$  and  $B'$ ; and if this is the position of balance the resistance of the cell can be read off directly from the box,  $R_1$  (assuming, of course, that  $R_3 = R_4$ ). But if  $B'$  must be moved along the scale to obtain a balance, then resistance is being added to  $R_1$  and subtracted from  $R_2$ , and by proper calibration the reading of  $B'$  on the scale can be added to the reading of the box  $R_1$  to give the actual resistance of the cell. This makes the bridge direct reading even down to a few thousandths of an ohm. Although the direct-reading bridge has the great advantage of saving time, still more important is the fact that it permits an immediate appreciation of the significance of the measurements.

The adjustment of the sliding contact,  $B$ , so as to make  $R_3$  equal to  $R_4$  is accomplished with the help of two extra 100-ohm coils, which have been adjusted so as to make them very nearly equal. After these have been connected across the gaps  $AM$  and  $A'N$ , respectively, and the slider,  $B'$ , has been set at zero, the bridge is balanced by moving the slider,  $B$ , and its position is noted on the scale. The two 1000-ohm resistances are then interchanged, the bridge is again balanced by moving  $B$ , and its position is again noted. The midpoint between the two positions will be the true midpoint of the ratio arms. The slider,  $B$ , is then clamped in this position, thus making the ratio arms exactly equal. The true midpoint between  $M$  and  $N$  is then obtained by placing heavy links of equal and negligible resistance across  $AM$  and  $A'M$  and moving  $B'$  until the bridge is in balance. The reading is brought to zero by loosening the scale on its shaft by turning its set screw, and moving it to the proper point without moving the slider, when it is tightened again.

(c) *Variable Resistances.* Various forms of variable resistance are used in conductance measurements. A simple type consists of a box containing coils of resistance wire arranged in sets of nine, the value of the resistance of each coil in a particular set being the same and one-tenth of the value of each coil in the preceding set. The coils are thrown into the circuit by means of dial switches located on top of the box (Fig. 25), thus permitting convenient and rapid manipulation.

The alternating-current errors inherent in the variable resistances usually employed in conductance measurements have been carefully determined by Jones and Josephs,<sup>1</sup> who have found them to be generally negligible below 1000 ohms but to increase with the resistance. These

<sup>1</sup> *J. Am. Chem. Soc.*, **50**, 1049 (1928).

errors are negative and also increase with the frequency of the current, indicating that the cause is dielectric loss in the insulator. As a result of their experimental and theoretical analysis, these investigators conclude that the variable resistance should meet the following specifications:

1. The resistance of each coil or any combination as mounted in the box and selected by switches should be the same (within 0.001 per cent) with direct current as with alternating current of any frequency up to the maximum used (say 3000 cycles per second), and the reactance should be as low as possible. As one of the conditions necessary for meeting this specification, coils of 10,000 ohms or more must be entirely disconnected from the circuit when not in use.

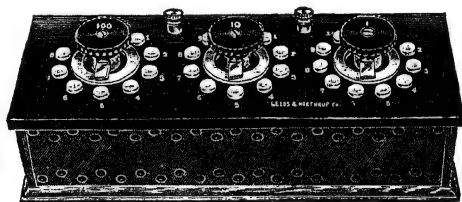


Fig. 25.

2. The temperature coefficient of the resistance box should be low, constant, and known.

3. For convenience the box should be of the decade type with dial switches, in order that the bridge may be made direct reading by use of equal ratio arms. A box of six decades, reading in tenths, units, tens, hundreds, thousands, and ten thousands of ohms, has a desirable range and precision.

4. The contact resistance in the switches and the resistance of the lead wires should be made as small as possible and should not vary by more than 0.001 ohm during use.

5. The switch terminals and lead wires connecting the coils and terminals must be so designed that the lead wires are included in the value of each coil in exactly the same manner for all settings of the switch.

In Fig. 26 is shown diagrammatically the top of a resistance box meeting these specifications.

(d) *Sources of High-Frequency Alternating Currents.* Various sources of electromotive force are employed in measurements of electrolytic conductance. In order to reduce electrolytic disturbances and polarization effects to a minimum, a source producing a high-frequency alternating current should usually be employed. The two most commonly used

sources of power are the microphone hummer, which delivers current at a constant frequency of 1000 cycles, and the audion tube oscillator which produces current at several high frequencies. The microphone hummer is suitable for student and routine work. The audion tube oscillator is

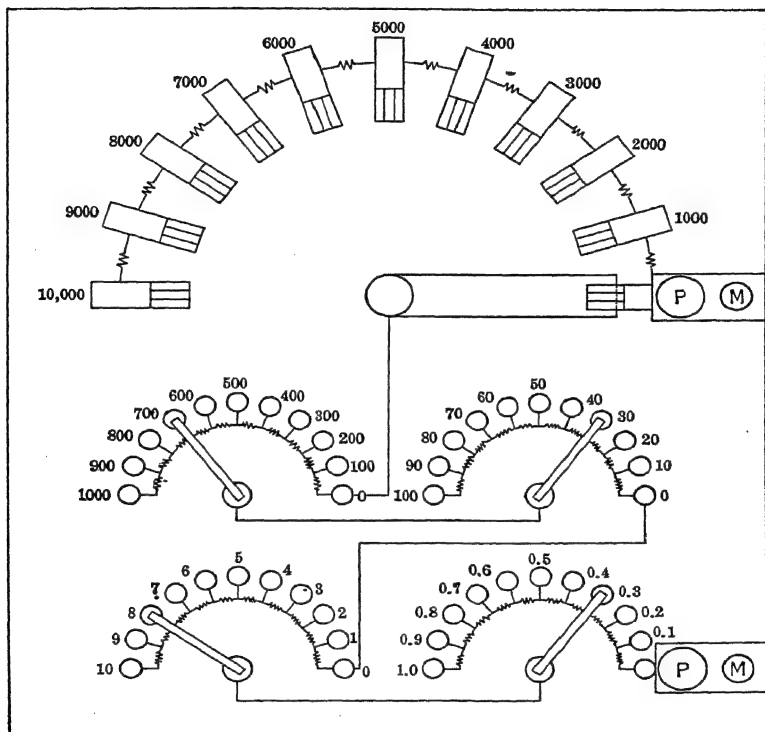


FIG. 26.

required for research and precise laboratory work; it is described on p. 82.

The results of a theoretical study led Debye and Falkenhagen<sup>1</sup> to conclude that at high frequencies the conductance should increase with the frequency. Variations of conductance with frequency, of the order of the experimental error of the method used, were observed by Sack<sup>2</sup>

<sup>1</sup> *Physik. Z.*, **29**, 121 (1928); cf. Falkenhagen and Williams, *J. Phys. Chem.*, **33**, 1121 (1929); Falkenhagen and Fleischer, *Physik. Z.*, **39**, 305 (1933). A review of work on this subject is given by Deubner, *Physik. regelm. Ber.*, **8**, 97 (1940).

<sup>2</sup> *Physik. Z.*, **29**, 627 (1928).

at frequencies between six million and twenty million cycles per second. On the other hand, Jones and Josephs<sup>1</sup> found that this change in conductance is no greater than a few thousandths of 1 per cent between the limits of 1090 and 4000 cycles per second, when errors due to polarization and capacitative shunt are avoided; and Richardson<sup>2</sup> showed that the conductance of electrolytes is independent of the frequency up to 8 megacycles per second.

(e) *The Telephone.* A properly constructed telephone receiver, which is tuned<sup>3</sup> to the frequency of the alternating current employed, has

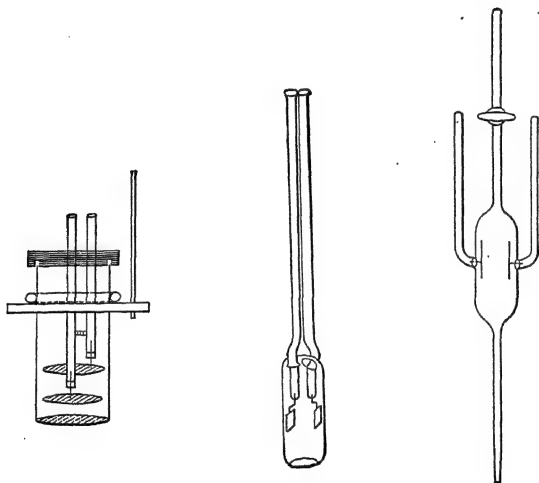


FIG. 27.

been found<sup>4</sup> to be greatly superior to all other instruments that have been proposed for determining the setting of the alternating-current bridge. Telephones can be readily obtained with an audibility current not greater than  $10^{-9}$  ampere, audibility current being defined as the least current through the telephone which will produce an audible tone. To obtain the maximum sensitiveness, the impedance should equal that of the bridge.

As a result of advances in the field of electronics, two new tools are now available as substitutes for the telephone. The "electric eye" has

<sup>1</sup> *Loc. cit.*

<sup>2</sup> *Phys. Rev.*, **35**, 297 (1930).

<sup>3</sup> A method of tuning the telephone is described by Washburn and Parker, *J. Am. Chem. Soc.*, **39**, 238 (1917).

<sup>4</sup> Washburn and Parker, *loc. cit.*

been suggested <sup>1</sup> as a detector in conductance measurements, and the cathode-ray oscillograph has been proposed <sup>2</sup> for this purpose and used <sup>3</sup> with most satisfactory results.

(f) *Conductance Cells.* Several of the commoner types of conductance cells are shown in Fig. 27. These cells usually consist of a glass vessel in which are placed two platinum electrodes. The relative position of the electrodes is fixed, either by cementing the electrodes to the cover of the cell or by joining them together by a short piece of glass rod. Before using, the conductance cell should be thoroughly cleaned with a mixture of potassium bichromate and sulphuric acid, washed with distilled water, and finally inverted for a short time over a glass tube from which steam issues.

The theory and design of conductance cells were considered by Washburn,<sup>4</sup> who found that: "the area of the cross-section between the electrodes must not be less than a certain minimum value which is completely fixed and determined by the audibility current <sup>5</sup> of the telephone, the time required to make the bridge setting, the lowest specific conductance which it is desired to include within the range of the cell, and the percentage accuracy demanded in the measurements. This practically means that conductance cells should be designed to fit the telephone receiver which is to be employed with them." The theory and design of conductance cells have also been considered by Shedlovsky <sup>6</sup> and by Jones and Bollinger,<sup>7</sup> who have found that, in the type of cell commonly used, the measured resistance is lower than the true resistance of the electrolyte between the

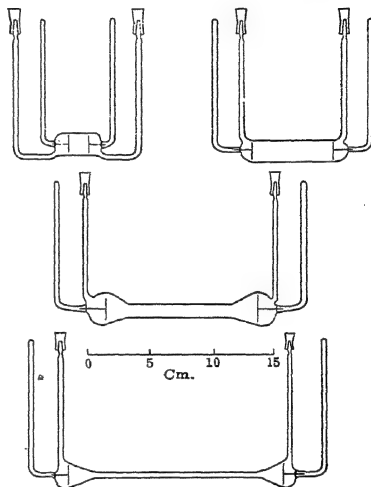


FIG. 28.

<sup>1</sup> Hovorka and Mendenhall, *J. Chem. Education*, **16**, 239 (1939). A wiring diagram is included in this paper.

<sup>2</sup> Lamson, *Rev. Sci. Instruments*, **9**, 272 (1938); *Gen. Radio Experimenter*, **13**, No. 11 (1939).

<sup>3</sup> Jones, Mysels, and Juda, *J. Am. Chem. Soc.*, **62**, 2919 (1940).

<sup>4</sup> *J. Am. Chem. Soc.*, **38**, 2431 (1916).

<sup>5</sup> A method of determining the audibility current of a telephone receiver is described by Washburn and Parker, *J. Am. Chem. Soc.*, **39**, 243 (1917).

<sup>6</sup> *Ibid.*, **52**, 1806 (1930).

<sup>7</sup> *Ibid.*, **53**, 411 (1931).

electrodes. This is due to the capacitative shunt between parts of the cell of opposite polarity. The cells shown in Fig. 28 have been designed by Jones and Bollinger to eliminate this source of error.

(g) *The Elimination of Polarization.* The occurrence of polarization in the conductance cell is most undesirable, for, unless it is eliminated, it is not possible to obtain a sharp minimum in the telephone. In solutions of low conductance, the effects of polarization may be eliminated by balancing the capacity of the cell against a variable air condenser, placed in parallel with the variable resistance (see *K*, Fig. 21). With solutions having a high conductance, this method is not practical, owing to the magnitude of the capacity required. Polarization may also be eliminated by merely increasing the frequency of the alternating current until a sharp minimum is obtained in the telephone. The same result may be achieved by properly coating the electrodes with platinum black,<sup>1</sup> employing large electrodes and a high resistance. The efficacy of the platinum black is due largely to the increase brought about in the area of the electrodes, but partly to its catalytic powers.

Platinum electrodes can be platinized by placing them in a platinizing solution (consisting of 3 grams of platinic chloride, 0.02–0.03 gram of lead<sup>2</sup> acetate, and 100 cubic centimeters of water), and passing an electric current from two storage cells between them for ten to fifteen minutes. The strength of the current is so regulated that only a small amount of gas is evolved, and its direction is reversed every thirty seconds by means of a commutator. After the electrodes are coated with platinum black, they are thoroughly washed with distilled water. The last traces of chlorine absorbed by the electrodes may be removed by making the two electrodes cathode in a dilute solution of sulphuric acid, and passing an electric current between them and a platinum anode.<sup>3</sup>

(h) *Application of the Thermionic Amplifier to Conductance Measurements.* The use of the audion tube (thermionic) amplifier was suggested<sup>4</sup> to increase the sensitiveness of the telephone. By the introduction of this device into the bridge network a substantial reduction of the current through the bridge proper can be effected, thereby minimizing polarization and heating effects in the cell, and at the same time permitting a sensitiveness of one part per million in the bridge setting to be secured.

<sup>1</sup> For other methods of eliminating the effects of polarization, see Curtis and Taylor, *Phys. Rev.*, **6**, 64 (1915); Wolcott, *Ann. Physik*, **12**, 1653 (1903).

<sup>2</sup> Lead is added to facilitate the formation of platinum black instead of a bright platinum plate.

<sup>3</sup> Various criteria as to the quality and sufficiency of the platinization are discussed by Jones and Bollinger, *J. Am. Chem. Soc.*, **57**, 280 (1935).

<sup>4</sup> Hall and Adams, *ibid.*, **41**, 1515 (1919); Jones and Josephs, *ibid.*, **50**, 1049 (1928); Jones and Bollinger, *ibid.*, **51**, 2407 (1929).

In Fig. 29 is shown a diagrammatical arrangement of a simple bridge and an audion tube amplifier. In this figure  $V$  is an electron generator or audion, consisting of a metal plate  $P$ , a grid of fine wire  $G$ , and a filament  $F$ , which can be heated by means of a current from the filament battery  $B_1$ . The plate  $P$  is connected through the telephone  $T$  to the positive side of the plate battery  $B_2$ . The other side of this battery is joined to the filament. The amplifier is connected to the bridge shown in Fig. 24 at the terminals marked "Tel."

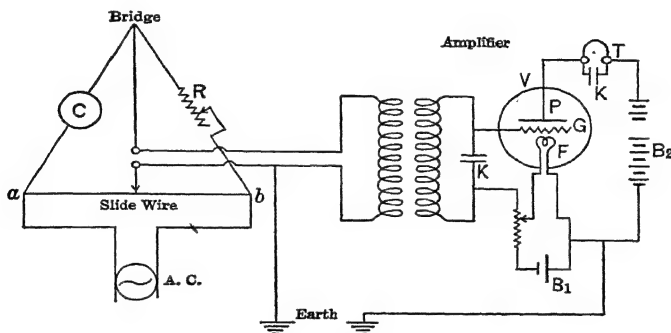


FIG. 29.

The principle on which the amplification of the high-frequency current from the bridge depends<sup>1</sup> is, briefly, as follows:

When the filament  $F$  is heated, it gives off electrons which move to the plate  $P$ , and a current flows through the plate battery circuit. This current is a function of both the plate and the grid potentials, but it is influenced more by the grid than by the plate potentials. This will be seen by referring to Fig. 30, which illustrates the manner in which the plate current changes with variations in both the plate and grid potentials. It will be observed that a given change in the grid potential produces a much greater variation in the plate current than does the same change in the plate potential. Accordingly, when the high-frequency current from the bridge produces periodic fluctuations of potential in the grid, the thermionic current from  $F$  to  $P$  changes simultaneously, and therefore the current through the telephone is increased or decreased. It is evident from the relations given in Fig. 30 that the current fluctuations in the telephone are greater, and therefore the sensitivity higher,

<sup>1</sup> A comprehensive discussion of the principle on which the thermionic amplifier operates will be found in van der Bijl's *Thermionic Vacuum Tubes*, Chapter VII, 1920.



than if the high-frequency current from the bridge had passed directly through the telephone. The bridge current may be further amplified by increasing the number of amplifier bulbs.

An audion tube oscillator for producing the high-frequency current used in conductance measurements has been recommended by a number of investigators.<sup>1</sup> A schematic wiring diagram of the oscillator is shown

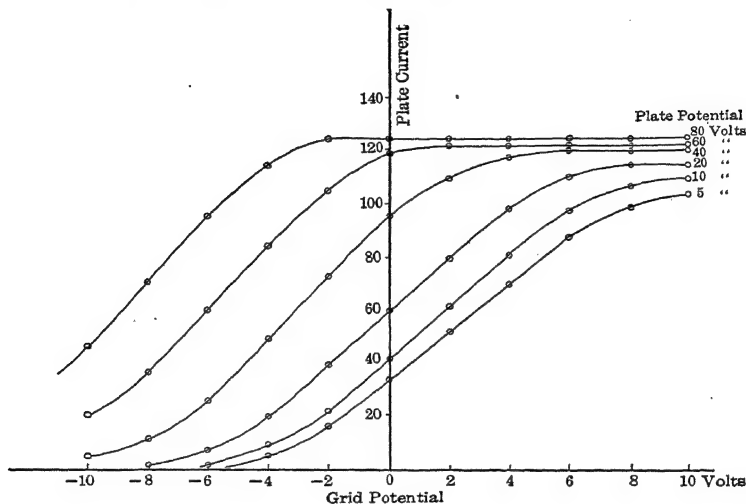


FIG. 30.

in Fig. 31. Although a first harmonic is present in the current, it does not cause trouble at frequencies above 1000 cycles per second. The frequency of the current is regulated by the condenser  $K$ , which is of small capacity and continuously variable over its entire range, and the condenser  $K'$ , which is variable in steps of, say, 0.005 microfarad. Currents of a few tenths to 25 amperes, having a frequency ranging from one-half to 50 million cycles, may be obtained from this type of generator.

The audion tube oscillator has several important advantages:<sup>2</sup> it is relatively cheap to build and operate, standard radio parts being used

<sup>1</sup> Hall and Adams, *J. Am. Chem. Soc.*, **41**, 1515 (1919); White, *Gen. Elec. Rev.*, **19**, 771 (1916), **20**, 635 (1917); Morecroft and Friss, *Trans. Am. Inst. Elec. Eng.*, **38**, 1193 (1919); Jones and Josephs, *J. Am. Chem. Soc.*, **50**, 1049 (1928). For improvements in oscillator design, see Jones and Bollinger, *ibid.*, **51**, 2407 (1929). The construction of a simple and inexpensive audion tube oscillator is described by Luder and Vernon, *J. Chem. Education*, **17**, 229 (1940).

<sup>2</sup> Jones and Josephs, *loc. cit.*

in its construction; its frequency and voltage are easily adjustable within the required limits, and its outside magnetic field is relatively small; it can be started and stopped conveniently and instantly, but it never stops of its own accord while in use.

(i) *Other Methods.* A differential method was proposed<sup>1</sup> for the measurement of electrolytic conductances. The apparatus (Fig. 32) employed in this method consists of a source of high-frequency alternating current  $I$ , a conductance cell  $C$ , a variable resistance  $R$ , a telephone  $T$ , and three coils,  $P_1$ ,  $P_2$ , and  $S$ , wound on an iron core. This

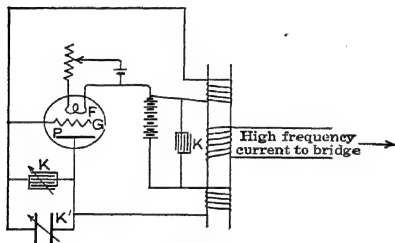


FIG. 31.

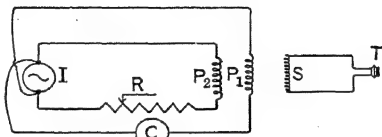


FIG. 32.

core is formed of two L-shaped pieces juxtaposed to form a rectangle;  $P_1$  and  $P_2$  are wound together on one long side, and  $S$ , composed of three separate coils, capable of being grouped variously, is wound on the opposite long side of the rectangle. The coils  $P_1$  and  $P_2$  have the same coefficient of auto-induction and resistance. Together the three coils form a differential transformer with two primary circuits and one secondary. The conductance cell and the variable resistance, which are placed in series with  $P_1$  and  $P_2$ , respectively, are both connected in such a way to  $I$  that the current at any instant flows through  $P_1$  and  $P_2$  in opposite directions. The coil  $S$  is joined directly to the telephone. When  $R$  is made equal to the resistance of the conductance cell, the electromotive force induced in  $S$  is zero and the telephone is silent. The sensitivity of the method is greatly increased by means of a thermionic amplifier.

Electrolytic conductances may also be measured by observing the drop in potential between two points in a tube containing the solution, during the passage of a direct current of known current strength.<sup>2</sup>

Redlich<sup>3</sup> attempted to avoid errors due to polarization by employing

<sup>1</sup> Rolla and Mazza, *Gazz. chim. ital.*, **52**, I, 421 (1922).

<sup>2</sup> Cf. Newberry, *J. Chem. Soc.*, **113**, 701 (1918); Eastman, *J. Am. Chem. Soc.*, **42**, 1648 (1920); Marie and W. A. Noyes, Jr., *ibid.*, **43**, 1905 (1921).

<sup>3</sup> *Z. physik. Chem.*, **136**, 331 (1928).

a double alternating-current potentiometer instead of a Wheatstone-Kohlrausch bridge.

**Conductance Water.** Ordinary water contains in solution substances which conduct the electric current. It is not suitable, therefore, for preparing solutions for conductance measurements. Water used for this purpose should have a very high degree of purity. Since pure water is a very poor conductor, the value of the specific conductance of water may be taken as a measure of its purity. Kendall<sup>1</sup> showed that, by distilling tap water to which a few cubic centimeters of Nessler's solution have been added, in Jena glass vessels and a block tin condenser, in contact with the air, water having a specific conductance of  $0.9 \times 10^{-6}$  mho at 25° can be obtained with one distillation. As this specific conductance is the same as that of pure water which has been saturated with carbon dioxide under atmospheric conditions (i.e., so-called "equilibrium water"), a permanent lower specific conductance for water in contact with the air is not possible, since carbon dioxide must be slowly absorbed until equilibrium is reached, unless air-tight vessels are used. According to Kendall, the aim should be to exclude all other conducting impurities except carbonic acid *and to make an exact correction for this*, rather than to attempt to prepare purer water than that saturated with carbonic acid. The method of deducing this correction will be discussed in Chapter XVII. With solutions which are not too dilute, and where a high degree of accuracy is not required, it often suffices to deduct the specific conductance of the solvent from that of the solution.<sup>2</sup>

The question of the magnitude and nature of the "water correction," and the influence of carbonic acid and the products to which this gives rise by metathesis, was critically examined by Washburn,<sup>3</sup> who concluded that it is necessary to employ very pure water, and to eliminate the influence of carbonic acid by making conductance measurements out of contact with the air. The data contained in Table XVI were presented by Washburn to illustrate the relative magnitudes of the "water correction" in conductance water of different degrees of purity. The figures in the third column show why it is impracticable to carry out conductance measurements in contact with air below concentrations of 0.0001 mole per liter, if the slightest uncertainty exists as to the exact value of the "water correction."

Water having a specific conductance of 0.05 to  $0.07 \times 10^{-6}$  mho at 18° ("ultra-pure" water) has been prepared in large quantities,<sup>4</sup> by

<sup>1</sup> *J. Am. Chem. Soc.*, **38**, 2460 (1916).

<sup>2</sup> For a comprehensive review of work on the "water correction," see Kendall, *ibid.*, **38**, 1480, 2460 (1916); **39**, 9 (1917).

<sup>3</sup> *Ibid.*, **40**, 106 (1918).

<sup>4</sup> Weiland, *ibid.*, **40**, 131 (1918).

heating ordinary conductance water ( $\kappa = 10^{-6}$  mho) to near its boiling point in a quartz still in a current of pure air (free from carbon dioxide and ammonia), the water vapor being condensed in a block tin condenser and collected in a quartz receiver. For the preparation of water having a specific conductance of  $0.05 \times 10^{-6}$  at  $18^\circ$ , a simple method which depends on fractional condensation has been recommended.<sup>1</sup>

TABLE XVI  
RELATIVE MAGNITUDES OF THE "WATER CORRECTION"

Concentration of KCl Mole per Liter	Specific Con- ductance of the Salt $\times 10^6$	Magnitude of the "Water Correction" in Per Cent of the Conductance of the Salt; for Water Having the Specific Conductance		
		$1 \times 10^{-6}$	$0.06 \times 10^{-6}$	$0.04 \times 10^{-6}$
0.000001	0.129	886.0	31.0	24.0
0.00001	1.296	44.0	4.4	3.0
0.0001	12.90	7.7	0.46	0.31
0.001	127.3	0.78	0.047	0.031
0.01	1224.0	0.082	0.0049	0.003
0.1	11200.0	0.009	0.00054	0.00036

**The Cell Constant.** It has been pointed out that the specific conductance of a solution is equal to the reciprocal of its resistance, measured between electrodes 1 square centimeter in area and 1 centimeter apart. If, as is usual in practice, the distance between the electrodes and their area differ from these values, the measured conductance will not be the specific conductance of the solution. Evidently, the specific conductance is related to the measured conductance by a constant factor depending upon the distance between the electrodes and their area. This factor, which is called the **cell constant** ( $K$ ), is equal to  $l/a$ , where  $l$  is the distance and  $a$  is the cross section of the solution between the electrodes. If we represent the measured conductance by  $c$ , then the specific conductance is equal to  $Kc$ . Accordingly, the cell constant may be determined for a particular cell by measuring the conductance of a solution of known specific conductance. Solutions of potassium chloride are most frequently employed for this purpose, and the specific conductances of these solutions have been determined with great accuracy. In Table XVII are given values of the specific conductance of potassium chloride

<sup>1</sup> Kraus and Dexter, *ibid.*, **44**, 2468 (1922).

solutions at the two temperatures most used in conductance measurements.<sup>1</sup>

Since the specific conductance of an electrolytic conductor increases about 2 per cent per degree rise in temperature, it is essential that conductance measurements should be made at a definite and constant temperature. This is accomplished by immersing the conductance cell,

TABLE XVII  
SPECIFIC CONDUCTANCE OF KCl \*

Grams KCl per 1000 grams solution <i>in vacuo</i>	Specific Conductance	
	18° C	25° C
71.1352	0.097838	0.111342
7.41913	0.0111667	0.0128560
0.745263	0.00122052	0.00140877

\* Jones and Bradshaw, *J. Am. Chem. Soc.*, **55**, 1799 (1933).

in a thermostat. The variation in the temperature of the thermostat should not exceed 0.05° to 0.1°, and where high accuracy is desired, it should not exceed 0.01°.

It was observed by Parker<sup>2</sup> that the ratio of the resistances of two cells containing a common solution and measured with an alternating-current bridge varies with the specific conductance of the solution employed, indicating that the cell constant does not have a fixed value at a constant temperature—an assumption which is vital for the Kohlrausch bridge method. This variation of the cell constant with the conductance of the solution is known as the Parker effect. Although Jones and Bollinger<sup>3</sup> confirmed this effect for the types of cells commonly employed, they showed experimentally that the value of the ratio is independent of the conductance of the solution when the conductance measurements are made with cells of proper design.

**Calculation of the Equivalent Conductance.** If the bridge wire is divided into 100 parts and  $x$  is the reading at the position of minimum

<sup>1</sup> See also Bremner and Thompson, *J. Am. Chem. Soc.*, **59**, 2372 (1937).

<sup>2</sup> *Ibid.*, **45**, 1366, 2017 (1923).

<sup>3</sup> *Ibid.*, **53**, 411 (1931).

sound, then the resistance,  $C$ , of the solution is given by the expression

$$C = \frac{R(100 - x)}{x}$$

whence the observed conductance of the solution is

$$c = \frac{1}{C} = \frac{x}{R(100 - x)} \quad (4)$$

Since the specific conductance is equal to  $Kc$ , it follows that

$$\kappa = \frac{K}{R} \cdot \frac{x}{(100 - x)} \quad (5)$$

On combining equation 5 with equation 2 we obtain for the equivalent conductance the expression

$$\Lambda = \frac{K}{R} \cdot \frac{x}{(100 - x)} \cdot \phi \quad (6)$$

Similarly, the molar conductance is given by the equation

$$\mu = \frac{K}{R} \cdot \frac{x}{(100 - x)} \cdot \phi \quad (6a)$$

**The Change of Conductance with Concentration.** Since the conductance of a solution depends on the number of ions present, the specific conductance must diminish as the concentration decreases. The manner in which both the specific and equivalent conductances vary with concentration is illustrated by the data in Table XVIII, for an aqueous and a non-aqueous solution of trimethyl-para-tolylammonium iodide at 25°. <sup>1</sup>

It will be observed from the data in the table that, although the specific conductance decreases, the equivalent conductance steadily increases as the concentration diminishes. Since the equivalent conductance of a given electrovalent solute depends upon the number of ions furnished by it and since this number is independent of the concentration, except in so far as an electrovalency may change over into a covalency, an increase in the equivalent conductance with decreasing concentration must mean that the number of ion pairs and the electrostatic forces retarding complete independence of ion movement must decrease, when one equivalent of the solute is contained in a larger than in a smaller volume. We should expect, however, the equivalent con-

<sup>1</sup> Creighton and Way, *J. Franklin Inst.*, **186**, 675 (1918).

TABLE XVIII

CHANGE OF SPECIFIC AND EQUIVALENT CONDUCTANCES WITH CONCENTRATION

Dilution * $V = \frac{1}{c} = \phi \times 10^{-3}$	Solution of Trimethyl-para-tolylammonium Iodide in:			
	Water		Formic Acid	
	$\kappa \times 10^3$	$\Lambda$	$\kappa \times 10^3$	$\Lambda$
32	2.950	94.4	1.605	51.4
64	1.550	99.2	0.937	60.0
128	0.804	102.9	0.511	65.4
256	0.413	105.6	0.280	71.7
512	0.2101	107.7	0.146	74.6
1024	0.1068	109.4	0.0765	78.3
2048	0.05415	110.9	0.0393	80.5

\* By the "dilution" ( $V$ ) of a solution is meant the reciprocal of its concentration. It is, therefore, the number of liters of solution which contains one equivalent (or mole) of solute.

TABLE XIX

CHANGE OF EQUIVALENT CONDUCTANCE WITH CONCENTRATION \*

Concentration	KCl	NaCl	AgNO <sub>3</sub>	KNO <sub>3</sub>	HCl
0.10	128.90	106.68	109.10	120.36	391.20
0.07	.....	.....	.....	123.52	395.33
0.05	133.33	110.88	115.20	126.27	398.97
0.02	138.34	115.67	121.37	132.37	407.12
0.01	141.32	118.45	124.72	135.78	411.88
0.005	143.64	120.60	127.16	138.44	415.75
0.002	145.79	122.64	129.32	140.54	419.27
0.001	146.93	123.71	130.47	141.80	421.24
0.0005	147.80	124.48	131.32	142.73	422.62
0.0002	148.56	125.19	132.08	143.53	423.86
0.0001	148.90	125.56	132.46	144.02	424.53
0	149.82	126.42	133.32	144.92	426.04

\* Shedlovsky, *J. Am. Chem. Soc.*, **54**, 1424 (1932).

ductance to attain a limiting value at very small concentrations, when the ions are so far apart that the electrostatic forces are negligible. This conclusion has been found to hold for many electrolytes. This limiting value of the conductance of an electrolyte is called its **equivalent conductance at zero concentration** ( $\Lambda_0$ ). Table XIX illustrates the change

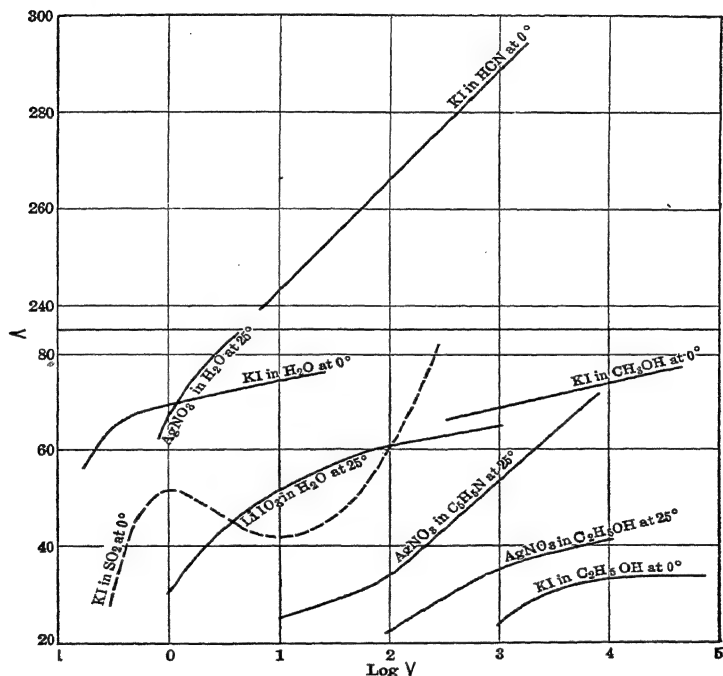


FIG. 33.

in the value of the equivalent conductance at 25°, over a wide range of concentration in aqueous solution.

The form of the equivalent conductance-concentration curves for solutions of several electrolytes is shown in Fig. 33.

Numerous functions have been proposed to express the relation between equivalent conductance and concentration.<sup>1</sup> The simple relation

$$\Lambda = \Lambda_0 - Ac^{\frac{1}{2}} \quad (7)$$

<sup>1</sup> A. A. Noyes, *Carnegie Institute Publ.*, **63**, 48 (1907), gives references to a number of early papers on this subject.



where  $c$  is the equivalent concentration and  $A$  is a constant, holds closely between  $c = 0.001$  and  $c = 0.1$  normal for many uniunivalent salts. For salts of this type the value of  $A$  varies between narrow limits, at  $18^\circ$  being about 400. Thus, for potassium chloride,  $\Lambda = 130 - 400\sqrt[3]{c}$ . With dilute solutions better results are obtained with the expression<sup>1</sup>

$$\Lambda = \Lambda_0 - Ac^{3/4} \quad (7a)$$

However, the values obtained with any of these functions, even when they contain three arbitrary constants, deviate considerably from the observed equivalent conductances at very low concentrations.<sup>2</sup> Much better results are obtained with the equation, containing four arbitrary constants, proposed by Kraus and Bray.<sup>3</sup> This equation, which has the form

$$\frac{(c\Lambda)}{c(\Lambda - \Lambda_0)} = K + D(c\Lambda)^m \quad (8)$$

where  $K$ ,  $D$ ,  $m$ , and  $\Lambda_0$  are constants, expresses satisfactorily the equivalent conductances of many non-aqueous solutions from very low concentrations up to  $0.5 N$ .

While the equivalent conductance of most aqueous and many non-aqueous solutions increases over a wide range of concentration as the dilution increases, the reverse behavior sometimes occurs,<sup>4</sup> especially in non-aqueous solutions (see the curve for KI in  $SO_2$ , Fig. 33). This phenomenon, known as **anomalous dissociation**, was studied extensively by Sachanov and his associates.<sup>5</sup> Although various factors, such as the viscosity of the solution, the volume occupied by the solute, changes in the velocities of the ions, and complex formation between solute and solvent, probably play a part in anomalous dissociation, undoubtedly the phenomenon is closely associated with the magnitude of the dielectric constant of the solvent medium.

It was suggested<sup>6</sup> that decrease in the equivalent conductance with concentration was related to a change in the dielectric constant of the

<sup>1</sup> Kohlrausch, *Z. Elektrochem.*, **13**, 333 (1907).

<sup>2</sup> For a discussion of these functions, the reader is referred to A. A. Noyes and Falk, *J. Am. Chem. Soc.*, **34**, 480-5 (1912).

<sup>3</sup> *Ibid.*, **35**, 1315 (1913). See also Shedlovsky, *ibid.*, **54**, 1411 (1932).

<sup>4</sup> See, for example, Fitzgerald, *J. Phys. Chem.*, **16**, 621 (1912); Darby, *J. Am. Chem. Soc.*, **40**, 347 (1918); Elsey, *ibid.*, **42**, 2454 (1920); Kraus and Kurtz, *ibid.*, **44**, 2463 (1922); Fuoss and Kraus, *ibid.*, **55**, 2387 (1933).

<sup>5</sup> *J. Russ. Phys. Chem. Soc.*, **43**, 543 (1911); **44**, 324 (1912); **45**, 102 (1913); **47**, 849, 859 (1915); *Z. Elektrochem.*, **19**, 588 (1913); **20**, 529 (1914); *J. Phys. Chem.*, **21**, 169 (1917). See also Rabinowitsch, *Z. physik. Chem.*, **99**, 338, 417, 434 (1921).

<sup>6</sup> Cf. Dhar, *Z. Elektrochem.*, **22**, 251 (1916).

solution during dilution, this change being more pronounced in solvents having low dielectric constants. Indeed, Walden<sup>1</sup> showed that the dielectric constant of a solution of tetraethylammonium chloride in chloroform ( $\epsilon = 4.95$ ) at first rapidly decreased with concentration:

$c = 1.0$	0.5	0.2	0.1	0.025 normal
$\epsilon = 28.8$	15.9	9.3	7.05	5.0

Consequently, the dissociating power of the solution and, therefore, the value of the equivalent conductance would diminish with dilution.

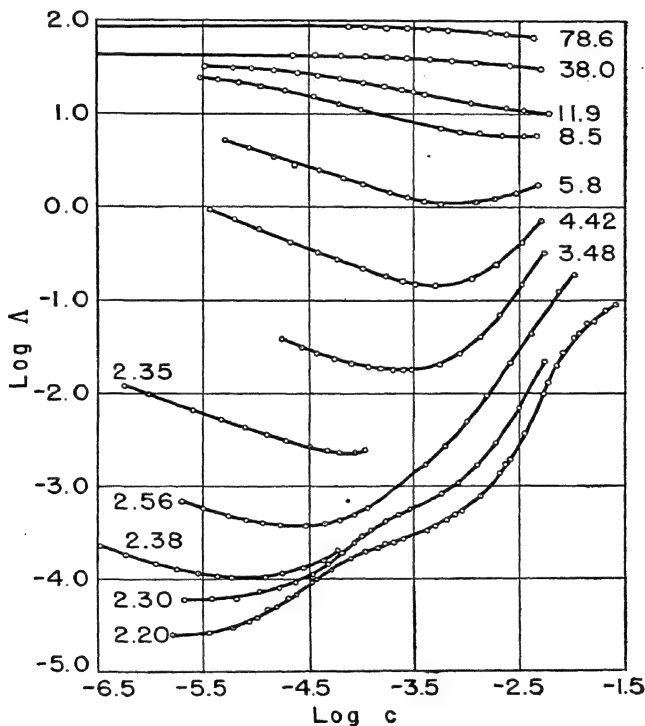


FIG. 34.

Kraus and Fuoss<sup>2</sup> studied the conductance of tetraisoamylammonium nitrate in dioxane-water mixtures having dielectric constants progressively decreasing from that of water (78.6) to that of dioxane (2.20).

<sup>1</sup> *Bull. Acad. Sci. St. Petersburg*, 1912, 305, 1055.

<sup>2</sup> *Loc. cit.*

These investigators found that, as the dielectric constant of the solvent medium was decreased, a point was reached at which the equivalent conductance-concentration curve passed through a minimum and that then this minimum shifted gradually towards lower concentrations, as shown in Fig. 34.<sup>1</sup> In this figure the value of the dielectric constant of the solvent medium is placed adjacent to the corresponding curve.

Walden discussed<sup>2</sup> the influence of the viscosity of the solution, the dielectric constant of the solvent, and the velocity of the ions on the form of the  $\Lambda$ - $V$  curve. He found that the dilution ( $V_m$ ) at which the  $\Lambda$ - $V$  curves exhibited a minimum was given by the expression

$$V_m = \left( \frac{\text{constant}}{\epsilon} \right)^3 \quad (9)$$

The value of the constant, which is independent of the nature of the solvent, varies between 33 and 38 (at 25°), according to the nature of the solute. With solvents having dielectric constants greater than the value of the constant in equation 9, it is evident that the  $\Lambda$ - $V$  curve passes through a minimum only in very concentrated solutions, and that at the concentrations usually employed in conductance measurements the values of  $\Lambda$  will steadily increase with dilution.

Walden has shown that, in calculating the equivalent conductance, not only the viscosity of the solution (see later) but also the volume ( $\phi'$ ) occupied by the solute must be taken into consideration, and that the corrected value of the equivalent conductance is given by the expression

$$\Lambda = \kappa \frac{\eta}{\eta_0} (\phi - \phi') \quad (10)$$

where  $\phi'$  is equal to the equivalent weight of the solute divided by its density. For dilute solutions, this equation reduces to equation 2.

**The Law of the Independent Migration of Ions.** Since in electrolytic conductors the electric current is carried by the ions, it follows, for equal concentrations of ions of the same valence, that that solution containing the faster-moving ions will be the better conductor. Obviously, at infinite dilution, when the ions are so far apart as to exert no influence on one another, the conductance will depend solely on the velocities of the anion and cation.

If  $u$  and  $v$  centimeters per second represent the velocity of the cation and anion, respectively, under a potential gradient of 1 volt per centimeter, then in a solution containing one equivalent of a uniunivalent

<sup>1</sup> See Kraus, *J. Franklin Inst.*, **225**, 692 (1938).

<sup>2</sup> *Z. physik. Chem.*, **100**, 512 (1922).

electrolyte at infinite dilution,  $uF$  coulombs of positive electricity will be transported by the cations in 1 second, and  $vF$  coulombs of negative electricity will be transported by the anions in the same time. Hence the total current flowing through the solution will be:

$$I = \frac{1}{R} = \Lambda_0 = uF - v(-F) = (u + v)F \quad (11)$$

coulombs per second, or amperes. The quantities  $u$  and  $v$  are sometimes called the **mobilities** of the ions. Since the velocities of the ions are entirely characteristic, it follows that the values of the equivalent conductance at zero concentration of different electrolytes must be purely additive. This additive relationship was discovered by Kohlrausch, and is called Kohlrausch's law or the **law of the independent migration of ions**. It follows from this law that the differences in the value of  $\Lambda_0$  for salts of the same cation or anion must be the same. This is shown by Table XX, in which are given the equivalent conductances

TABLE XX

## KOHLEAUSCH'S LAW

Anion (X)	K Salt $\Lambda_0 = (u_{K^+} + v_{X^-})F$	Na Salt $\Lambda_0 = (u_{Na^+} + v_{X^-})F$	$(u_{K^+} - u_{Na^+})F$
F <sup>-</sup>	111.2 (18.8)	90.1 (18.8)	21.1
Cl <sup>-</sup>	130.0 (31.5)	108.9 (31.5)	21.1
IO <sub>3</sub> <sup>-</sup>	98.5 (27.8)	77.4 (27.8)	21.1
NO <sub>3</sub> <sup>-</sup>	126.3	105.2	21.1

at zero concentration <sup>1</sup> of a number of sodium and potassium salts at 18°. The difference between the equivalent conductances of sodium and potassium salts of the same anion is given in the fourth column of the table. The bracketed values represent the difference between the equivalent conductances of sodium and potassium salts of adjacent anions.

From a critical survey of existing data, Boizard <sup>2</sup> found that the law of the independent migration of ions held remarkably well for aqueous solutions of many salts, such as chlorides, nitrates, and sulphates. Kohlrausch's law has been found to hold also for a number of non-aqueous solutions. As early as 1897, Carrara <sup>3</sup> observed that the halogen

<sup>1</sup> A. A. Noyes and Falk, *J. Am. Chem. Soc.*, **34**, 454 (1912).

<sup>2</sup> *J. phys.*, **3**, 701 (1913).

<sup>3</sup> Cf. *Atti accad. Lincei*, **4**, 339 (1901).

ions have the same velocity in methyl alcohol as in water, and that the sodium and potassium ions have the same velocities when calculated from their different halogen salts. In other words, Kohlrausch's law applies to these solutions. The law was also verified <sup>1</sup> for solutions of a number of solutes in acetonitrile and epichlorohydrin. Dutoit and Gyr <sup>2</sup> showed that the values of the equivalent conductance of sulphur dioxide solutions of the bromides and iodides of potassium, rubidium, ammonium, and tetraethylammonium conformed with the law of the independent migration of ions. On the other hand, solutions in a number of solvents have been studied for which apparently the law of the independent migration of ions does not hold even approximately.

Since the magnitude of the equivalent conductance at zero concentration depends wholly on the velocities of the ions, it follows that this gives a measure of the magnitude of the ionic mobilities. From the fact that in aqueous solution the equivalent conductance of acids and bases is much higher than that of other electrolytes in the same solvent (see Table XIX), we may infer that the velocities of the hydrogen and hydroxyl ions are very much greater than those of other ions. For a particular electrolyte the magnitude of the equivalent conductance at zero concentration, and therefore of the ionic mobilities, depends on the nature of the solvent, as is shown by the data given in Table XXI for tetraethylammonium iodide <sup>3</sup> and trimethyl-para-tolylammonium iodide <sup>4</sup> at 25°. These data show that the presence of the benzene nucleus in the solvent brings about a very marked reduction in the velocities of the ions.

In view of their own results and those of other investigators, Dutoit and Friederich <sup>5</sup> concluded that, when the same electrolyte is dissolved in different solvents, the values of the equivalent conductance at zero concentration are direct functions of the association of the solvent, and inverse functions of its viscosity. Walden <sup>6</sup> found that the product of the viscosity of the solvent and the equivalent conductance at zero concentration of a large number of solutions is a constant quantity, i.e.,

$$\eta_0 \times \Lambda_0 = \text{constant} \quad (12)$$

<sup>1</sup> Walden, *Z. physik. Chem.*, **54**, 129 (1906).

<sup>2</sup> *J. chim. phys.*, **7**, 189 (1909).

<sup>3</sup> Walden, *Z. physik. Chem.*, **54**, 129 (1906). For an excellent summary of measurements of conductance in non-aqueous solutions, see Murray-Rust, Gatty, Macfarlane, and Hartley, *Chem. Soc. Ann. Reports*, **1930**, 337-42.

<sup>4</sup> Creighton and Way, *J. Franklin Inst.*, **186**, 675 (1918).

<sup>5</sup> *Bull. soc. chim.*, **19**, 321 (1898).

<sup>6</sup> *Z. physik. Chem.*, **55**, 207 (1906); *Z. anorg. Chem.*, **113**, 85 (1920).

The value of this constant depends upon the nature of the solute, but it is independent of the nature of the solvent and, since the temperature coefficients of conductance and fluidity ( $1/\eta_0$ ) are practically equal, the temperature. For binary electrolytes the value of the constant varies between 0.5 and 1.0.

TABLE XXI

EQUIVALENT CONDUCTANCE AT ZERO CONCENTRATION IN DIFFERENT SOLVENTS

Solvent	Equivalent Conductance at Zero Concentration of:	
	$(\text{C}_2\text{H}_5)_4\text{NI}$	$\text{C}_7\text{H}_7\text{N}(\text{CH}_3)_3\text{I}$
Nitromethane.....	120	115
Nitrobenzene.....	40	38
Propionitrile.....	165	143
Benzonitrile.....	56.5	54
Propionaldehyde. . .	145	120
Benzaldehyde.....	42.5	33

**The Application of Kohlrausch's Law.** The equivalent conductance of many electrolytes rapidly approaches a limiting value with decreasing concentration (see Table XIX). Accordingly, the equivalent conductance at zero concentration of such electrolytes may be determined fairly accurately by direct measurement and extrapolation. On the other hand, the equivalent conductance of acetic acid and a large number of other electrolytes shows no evidence of converging to a limiting value, even at very low concentrations. The equivalent conductance at zero concentration of these substances may, however, be calculated with the aid of the law of the independent migration of ions. For example, if we add together the equivalent conductances at zero concentration of hydrochloric acid and potassium acetate, and subtract from the sum the equivalent conductance at zero concentration of potassium chloride, the result obtained is  $(u_{\text{H}^+} + v_{\text{Ac}^-})F$ , or the equivalent conductance at zero concentration of acetic acid (HAc). Expressed mathematically

$$(u_{\text{H}^+} + v_{\text{Cl}^-})F + (u_{\text{K}^+} + v_{\text{Ac}^-})F - (u_{\text{K}^+} + v_{\text{Cl}^-})F = (u_{\text{H}^+} + v_{\text{Ac}^-})F$$

or

$$\Lambda_0(\text{HCl}) + \Lambda_0(\text{KAc}) - \Lambda_0(\text{KCl}) = \Lambda_0(\text{HAc})$$

In general, the equivalent conductance at zero concentration of any binary electrolyte, MA, is equal to the sum of the equivalent conductances at zero concentration of any two electrolytes, MA' and M'A, minus the equivalent conductance at zero concentration of the electrolyte M'A'.

**The Relation between Equivalent Conductance and Dissociation.** We have seen that the equivalent conductance of a binary electrolyte at zero concentration is given by equation 11:

$$\Lambda_0 = (u + v)F$$

At any other concentration,  $c$ , its equivalent conductance would be

$$\Lambda_c = (u_c + v_c)F\alpha \quad (13)$$

where  $u_c$  and  $v_c$  are the velocities of the cation and anion, respectively, under a potential gradient of 1 volt per centimeter at the concentration  $c$ , and  $\alpha$  is the fraction of an equivalent of solute existing as independent ions. If now it may be assumed that the mobilities of the ions are independent of the concentration, then by dividing equation 13 by equation 11, we obtain

$$\alpha = \frac{\Lambda_c}{\Lambda_0} \quad (14)$$

the so-called **conductance ratio**, as a measure of the degree of dissociation. On account of the attractive forces between the ions and of the higher viscosity of the medium at finite concentrations, it is evident that the values obtained for the degree of dissociation by equation 14 will be too low.

A correction has been made for the variation in the viscosity of the medium on the assumption that, in accordance with Stokes' law, the velocities of the ions are inversely proportional to the viscosity of the medium through which they move, and consequently

$$\alpha = \frac{\Lambda_c}{\Lambda_0} \cdot \frac{\eta_c}{\eta_0} \quad (15)$$

where  $\eta_c$  and  $\eta_0$  represent the viscosity of the solution and the pure solvent, respectively. However, since the assumption of the equality of  $(u + v)$  and  $(u_c + v_c)$  is certainly not justifiable, equations 14 and 15 cannot be expected to give more than an approximate value for the degree of dissociation, except in very dilute solution. With electrolytes of higher types these equations give even less correct results since, on

account of the formation of intermediate ions, there are present in solution more than two ionic species, except at very low concentrations.<sup>1</sup>

Values of the conductance ratio,  $\frac{\Lambda_c}{\Lambda_0} \cdot \frac{\eta_c}{\eta_0}$ , for a number of typical salts in aqueous solution at 18° are given in Table XXII,<sup>2</sup> and the apparent percentage dissociations of several acids and bases at the same temperature are tabulated in Table XXIII.

From the data contained in Table XXII, it is seen that salts of the same general type have the same apparent dissociation at the same concentrations, and that it is always less than 100 per cent, even at 0.001 normal concentration. Although, undoubtedly, the concentrations of the ions in solutions of strong electrolytes are reduced either *apparently*, owing to rearrangements in their distribution, leading in some cases to the formation of ion pairs, or *actually*, owing to a change from an electrovalency to a covalency, the extent of this reduction is much smaller at higher concentrations than is indicated by the values of the conductance ratio given in the table. The results of light-absorption measurements by von Halban<sup>3</sup> and those of refractometric measurements by Fajans<sup>4</sup> support the view that it is probable that the proportion of "undissociated" molecules (i.e., associated ions and covalent molecules) does not exceed 5 per cent in aqueous solutions of strong electrolytes as concentrated as 5 normal, and that in not too concentrated solutions the electrovalent linkage is always dissociated to the same almost complete extent.

**The Dissociation of Weak Electrolytes.** On examining the data given in Table XXIII, it is observed that whereas the apparent dissociation of hydrochloric acid, nitric acid, and sodium hydroxide is approximately the same as that of uniunivalent salts at the same concentration, the apparent dissociation of the weak electrolytes, acetic acid and ammonium hydroxide, is of a much smaller order of magnitude, even though their salt, ammonium acetate, is practically completely dissociated in aqueous solution. The very small concentration of ions yielded by weak electrolytes, such as acetic acid, is attributed to the existence of the electrolyte in solution in two forms which are in equilibrium with each other: a covalent form and an electrovalent form, the proportion of the covalent greatly predominating. If, as there is reason to believe, the electrovalent linkage is always apparently dissociated to an extent of 83 per cent in 0.1 normal aqueous solution (see the uniunivalent salts in

<sup>1</sup> Cf. Lorenz, *Z. anorg. Chem.*, **106**, 49; **109**, 63 (1919).

<sup>2</sup> A. A. Noyes and Falk, *J. Am. Chem. Soc.*, **34**, 454 (1912).

<sup>3</sup> *Z. physik. Chem.*, **132**, 401, 433 (1928).

<sup>4</sup> *Trans. Faraday Soc.*, **23**, 357 (1927).



TABLE XXII

VARIATION OF CONDUCTANCE RATIO  $\times 100$  WITH CONCENTRATION

Salt	Concentration in Gram Equivalents per Liter									
	0.001	0.002	0.005	0.01	0.02	0.05	0.1	0.2	0.5	1.0
NaCl	97.7	96.9	95.3	93.6	91.6	88.2	85.2	81.8	77.3	74.1
KCl	97.9	97.1	95.6	94.1	92.2	88.9	86.0	82.7	77.9	74.2
KBr	97.8	97.0	95.5	94.0	92.1	88.8	85.9	82.5	76.6	....
NaNO <sub>3</sub>	97.7	96.8	95.0	93.2	91.0	87.1	83.2	78.8	71.9	66.0
LiNO <sub>3</sub>	97.5	96.5	95.0	93.2	91.1	87.4	84.0	80.3	75.0	70.3
AgNO <sub>3</sub>	97.7	96.8	95.0	93.1	90.8	85.9	81.4	....	....	....
Univalent:	98			93			83			
MgSO <sub>4</sub>	87.3	82.3	74.0	66.9	59.6	50.6	44.9	40.3	....	34.9
ZnSO <sub>4</sub>	85.4	79.9	71.0	63.3	55.6	46.4	40.5	36.0	....	30.9
CuSO <sub>4</sub>	86.2	80.4	70.9	62.9	55.0	45.5	36.9	35.1	....	30.9
Bivalent:	86			65			41			
CaCl <sub>2</sub>	95.4	93.8	91.0	88.2	84.9	80.2	76.4	72.7	68.6	66.2
MgCl <sub>2</sub>	95.5	93.9	91.0	88.3	85.1	80.3	76.5	72.8	68.7	66.9
K <sub>2</sub> SO <sub>4</sub>	95.4	93.7	90.5	87.2	83.2	77.1	72.2	67.3	61.8	59.2
Univalent:	95			87						

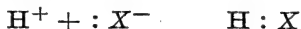
TABLE XXIII

APPARENT PERCENTAGE DISSOCIATION OF ACIDS AND BASES AT 18°

Electrolyte	Concentration in Gram Equivalents per Liter						
	0.001	0.002	0.005	0.01	0.02	0.05	0.1
HCl	99.0	98.6	98.1	97.2	95.7	94.4	92.0
HNO <sub>3</sub>	99.0	98.6	....	96.9	....	93.8	92.0
CH <sub>3</sub> CO <sub>2</sub> H	11.7	8.6	5.7	4.17	3.0	1.8	1.34
NaOH (25°)	97.1	95.5	94.8	93.33	....	....	90.5
NH <sub>4</sub> OH	11.7	8.6	5.5	4.07	3.0	1.9	1.31

Table XXII), then since in a solution of this concentration acetic acid is apparently 1 per cent dissociated, about 99 per cent of the acid must exist in the covalent form.

The tendency of acids to assume the covalent form, and the loss of this tendency on replacement of the acidic hydrogen by metal, are attributed to the fact "that hydrogen occupies a peculiar position in that the number of electrons which the hydrogen ion needs for stability is two, which is the precise number that it gains when it passes from the ionized to the covalent state:



But a metallic ion needs eight, and the condition of a metallic ion to which only two shared electrons have been added (as in sodium ethide) is excessively unstable. Hence the transformation into the covalent link will be far easier with hydrogen than with metals, and acids must have a power of changing into the covalent form which is in general denied to metals."<sup>1</sup>

The nitrogen bases consist of an equilibrium mixture of covalent and electrovalent forms as long as a hydrogen atom is attached to the nitrogen atom, on account of the great tendency of hydroxyl to form a covalent union with hydrogen. When, for example, the hydrogen of trimeth-

ylammonium hydroxide,  $\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{N} \\ \diagdown \\ \text{CH}_3 \end{array} \begin{array}{l} \text{H}-\text{OH} \\ \diagdown \\ \text{CH}_3 \end{array}$  is replaced by a fourth

methyl group, the resulting tetramethylammonium hydroxide dissociates in water to as great an extent as sodium hydroxide.<sup>2</sup>

**Non-Aqueous Solutions and Fused Salts.** As a rule the extent of dissociation of electrolytes in non-aqueous solution is less than in aqueous solution, although this is not always true. The change in the apparent degree of dissociation, with concentration, of several salts in non-aqueous solutions is shown graphically in Fig. 35.

The study of the conductance of *fused salts* has been much less extensive than that of solutions. It is supposed that dissociation is complete in electrolytes of this type, the process of fusion merely breaking down the solid into its *pre-existing* ions. This conclusion is substantiated by the results of Walden's investigation<sup>3</sup> of the conductance of molten tetra-alkylammonium picrates.

<sup>1</sup> Quoted from *The Electronic Theory of Valency*, by N. V. Sidgwick, p. 96.

<sup>2</sup> For a detailed discussion of the dissociation of the nitrogen bases, see Sidgwick, *op. cit.*, pp. 96-8.

<sup>3</sup> *Z. physik. Chem.*, A157, 389 (1931).

In a study of fused mixtures, consisting of  $\text{AlCl}_3$  with different alkali halides, the specific conductance has been found to be additive.<sup>1</sup>

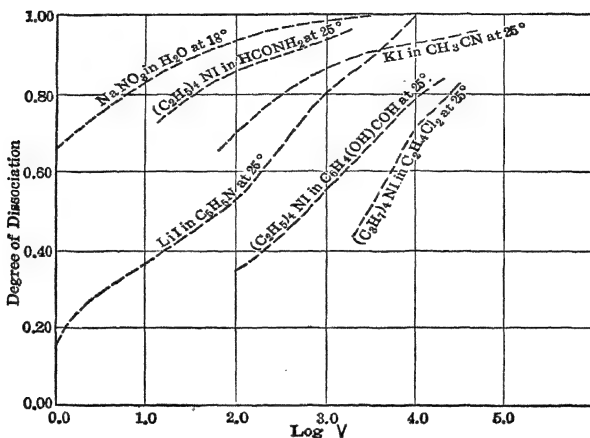


FIG. 35.

**Variation of the Conductance Ratio with Temperature.** At room temperature the variation of the conductance ratio with temperature is less than 0.1 per cent per degree. The change in this function for a number of electrolytes, in 0.08 normal aqueous solution, was determined over a wide temperature range by A. A. Noyes and his associates.<sup>2</sup> Their data, which are given in Table XXIV, show, for the electrolytes studied, that as the temperature increases the conductance ratio decreases, and that this is approximately the same for salts of the same ionic type. The decrease in the conductance ratio (expressed in percentage) per 10 degrees elevation in temperature ( $-10^3 \cdot d\alpha/dt$ , where  $\alpha = \Lambda_c/\Lambda_0$ ), in 0.08 normal aqueous solution, has for most salts the average values given in Table XXV. The decrease in the value of the conductance ratio with rising temperature is indicative of an increase in the association of the ions, which is probably due to the fact that the dielectric constant, and therefore the dissociating power, of all solvents decrease with rise in temperature. Accordingly, as the temperature is increased, we should expect the conductance ratio of various electrolytes

<sup>1</sup> Yamaguti and Sisido, *J. Chem. Soc. Japan*, **62**, 304 (1941). A new type of conductance cell for use with fused electrolytes has been described by these investigators, *ibid.*, **59**, 1311 (1938).

<sup>2</sup> *Carnegie Repts.*, **63**, 340 (1907); cf. Walden, *Z. physik. Chem.*, **106**, 49 (1923).

in aqueous solution to approach that of the same electrolytes in solvents having a lower dielectric constant. This is indeed the fact.

TABLE XXIV

CHANGE OF THE CONDUCTANCE RATIO WITH TEMPERATURE

Electrolyte	$\frac{\Lambda_c}{\Lambda_0} \times 100$					
	18°	100°	156°	218°	281°	306°
HCl	93.2	89.7	87.2	82.5	..	60
KCl	87.3	82.6	79.7	77.3	72	64
NaCl	85.7	83.2	81.2	77.7	69	63
AgNO <sub>3</sub>	83.3	80.2	75.8	70.8	60	57
NaC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	81.1	77.6	75.6	68.5	..	.....
K <sub>2</sub> SO <sub>4</sub>	73.2	64.8	58	45	31	23
Ba(NO <sub>3</sub> ) <sub>2</sub>	70.1	66.9	62	53	38	.....
MgSO <sub>4</sub>	45.5	31.9	19	7	..	.....
CH <sub>3</sub> CO <sub>2</sub> H	1.50	1.17	0.82	0.46	..	0.14

TABLE XXV

TEMPERATURE COEFFICIENT OF THE CONDUCTANCE RATIO

Type of Salt	Value of $(-10^3 \cdot d\alpha/dt)$ between				
	18° and 100°	100° and 156°	156° and 218°	218° and 281°	281° and 306°
Binary .....	0.32	0.55	0.68	1.09	2.84
Ternary .....	0.34	0.94	1.23	2.30	3.20

**Determination of the Equivalent Conductance at Zero Concentration.** Since the limiting value of the equivalent conductance is not reached even at the lowest concentrations at which conductance measurements have been made hitherto, it is customary to derive this value by extrapolation from values of the equivalent conductance at higher con-

centrations. This procedure is based on the assumption that the relations between the concentration and the equivalent conductance, which are found empirically to hold at higher concentrations, continue down to zero concentration. Extrapolation of conductance values to zero concentration may be carried out either graphically or algebraically by the substitution of two sets of data in some empirical function containing  $\Lambda$ ,  $\Lambda_0$ , and  $c$ . Thus, on putting equation 7 in the form

$$\Lambda_0 = \frac{\Lambda_2 \sqrt[3]{c_1} - \Lambda_1 \sqrt[3]{c_2}}{\sqrt[3]{c_1} - \sqrt[3]{c_2}} \quad (16)$$

values may be obtained for  $\Lambda_0$  by substituting in the equation values of  $\Lambda$  corresponding to successive values of  $c$ . Other empirical functions of this nature have been proposed by Kraus,<sup>1</sup> Kraus and Bray,<sup>2</sup> and others.<sup>3</sup>

Washburn, considering that none of these methods gives accurate values for  $\Lambda_0$ , proposed a new mode of procedure for ascertaining the true limiting value of the equivalent conductance.<sup>4</sup> This method consists in plotting  $\frac{\Lambda_c^2 \cdot c}{\Lambda_0(\Lambda_0 - \Lambda_c)} = K$  against  $c$  for assumed values of  $\Lambda_0$ ,

and rejecting such values of  $\Lambda_0$  as cause the curve to exhibit radical changes in direction in the region of very low concentrations. The

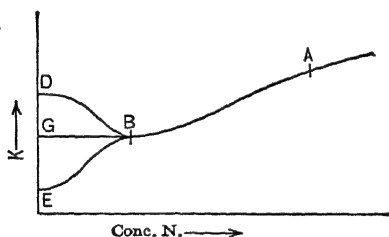


FIG. 36.

method rests on two assumptions:

(1) that with decreasing concentration the value of  $K$  decreases and approximates a constant value  $K_0$  at very low concentrations; and (2) that the relation between  $K$  and  $c$  must be such that in dilute solutions the curve does not exhibit any erratic behavior, such as a sudden rise or fall with decreasing concentration (i.e., that the deviations from the

law of mass action—see Chapter XIII—do not increase with dilution). Thus, if the curve (Fig. 36) runs from a point  $A$  to a point  $B$  at some low concentration, the value of  $\Lambda_0$  must be such that it does not proceed to either  $D$  or  $E$ , but continues smoothly to  $G$ . It is claimed that by this method  $\Lambda_0$  may be determined with an accuracy of  $\pm 0.01$  per cent,

<sup>1</sup> *Proc. Am. Chem. Soc.*, **1909**, 15. Cf. Fuoss and Kraus, *J. Am. Chem. Soc.*, **55**, 476 (1933).

<sup>2</sup> *J. Am. Chem. Soc.*, **35**, 1315 (1913).

<sup>3</sup> Lorenz, *Z. anorg. Chem.*, **108**, 81, 191 (1919).

<sup>4</sup> *J. Am. Chem. Soc.*, **40**, 122 (1918).

provided that the values of  $\Lambda$  employed are of this order of precision and extend to  $c = 0.00002$  normal.

According to the Ostwald-Bredig valence rule,<sup>1</sup> the value of  $\Lambda_0$  is related to the equivalent conductance at any concentration,  $c$ , by the formula

$$\Lambda_0 = \Lambda_c + z_1 z_2 d_c \quad (17)$$

where  $z_1$  and  $z_2$  are the valences of the anion and the cation, and  $d$  is a constant depending only on the concentration and the temperature. For a uniunivalent salt equation 17 reduces to

$$\Lambda_0 - \Lambda_c = d_c \quad (18)$$

This relation holds closely for sodium salts and chlorides at concentrations below 0.01 normal. If the difference,  $\Lambda_0 - \Lambda_c$ , is known for any sodium salt or chloride, then, by adding this difference to the  $\Lambda_c$  value of any other sodium salt or chloride, its equivalent conductance at zero concentration is obtained. Table XXVI gives the values of the difference,  $\Lambda_0 - \Lambda_c$ , obtained by Müller and Bauer<sup>2</sup> at different temperatures.

TABLE XXVI

VALUES OF  $\Lambda_0 - \Lambda_c$  AT DIFFERENT TEMPERATURES

$V = 100$		128	256	500	512	1000	1024
0°	3.8	3.5	2.5	1.8	1.8	1.3	1.3
18°	6.8	6.2	4.5	3.3	3.2	2.3	2.3
25°	8.1	7.3	5.3	3.9	3.8	2.75	2.7
35°	10.1	9.1	6.6	4.9	4.8	3.4	3.4
40°	11.1	10.0	7.3	5.4	5.3	3.8	3.8

The foregoing rule has no theoretical significance but depends on the fact that, at great dilutions, the conductance ratios of all salts are not very different, the difference being smaller the greater the dilution. Further, since the equivalent conductance at zero concentration has values which do not differ greatly for univalent chlorides and sodium salts, the difference,  $\Lambda_0 - \Lambda_c$ , must be approximately the same. However, the Ostwald-Bredig rule is not suitable for accurate extrapolation.

<sup>1</sup> Ostwald, *Z. physik. Chem.*, **1**, 75 (1887); **2**, 843 (1888); Bredig, *ibid.*, **13**, 197 (1894).

<sup>2</sup> *J. chim. phys.*, **2**, 495 (1904).

The limiting value of the equivalent conductance in both aqueous and non-aqueous solutions was discussed by Walden,<sup>1</sup> who showed that the Ostwald-Bredig rule was applicable to water and 15 organic solvents over a range of concentration extending from 0.004 to 0.00002 normal. From theoretical considerations, he deduced the relation

$$d_c \cdot \varepsilon \cdot \eta_0 = \text{constant} \quad (19)$$

where  $\varepsilon$  is the dielectric constant and  $\eta_0$  the viscosity of the solvent. On the introduction of the concentration factor,  $c^{0.45}$ , equation (19) assumes the form

$$\frac{d_c \cdot \varepsilon \cdot \eta_0}{c^{0.45}} = 51.4 \quad (20)$$

This relation holds for all solutes and solvents (including water) at all concentrations. Accordingly, if  $\varepsilon$  and  $\eta_0$  are known for a solvent,  $d_c = \Lambda_0 - \Lambda_c$  can be calculated for any concentration. Thence, from a single measurement of  $\Lambda_c$ , the value of  $\Lambda_0$ , and therefore the conductance ratio, can also be calculated.

By dividing both sides of equation 20 by  $\Lambda_0$ , and substituting  $\Lambda_0 - \Lambda_c$  for  $d_c$ , we obtain

$$\frac{\Lambda_0 - \Lambda_c}{\Lambda_0} \cdot \frac{\varepsilon}{c^{0.45}} = \frac{51.4}{\Lambda_0 \eta_0} \quad (21)$$

Since  $\Lambda_0 \eta_0$  is a constant (see equation 12) depending only on the nature of the solute, it follows that, if this product is known for a salt in any one solvent, the conductance ratio of the salt in any other solvent may be calculated. Although the foregoing relations are very broad, their application is limited by the fact that most of our values for the dielectric constants of solvents are far from accurate.<sup>2</sup>

**The Change in Conductance with Temperature.** The two factors which determine the form of the temperature-equivalent conductance curve are: (1) the increase in the viscosity of the solution, and the corresponding decrease in the mobility of the ions, with decreasing temperature; and (2) the increase in the association of ions with rising temperature. The temperature coefficient of conductance will be positive or negative, therefore, according as one or the other of these factors predominates. The relation between the temperature and the equivalent

<sup>1</sup> *Z. anorg. Chem.*, **113**, 113 (1920). Cf. Brodsky, *Z. physik. Chem.*, **108**, 293 (1924).

<sup>2</sup> Our knowledge of the dielectric constants of aqueous and non-aqueous solutions has been discussed by Walden and Ulich, *Z. physik. Chem.*, **110**, 43 (1924); Wyman, *Chem. Revs.*, **19**, 213 (1936).

conductance of aqueous solutions of strong electrolytes is given approximately by the expression

$$\Delta_t = \Delta_{18}[1 + \Delta(t - 18)] \quad (22)$$

where  $\Delta$  is the temperature coefficient. The magnitude of the temperature coefficient for dilute solutions at ordinary temperatures is illustrated by the values in Table XXVII.

TABLE XXVII  
TEMPERATURE COEFFICIENTS OF CONDUCTANCE

Type of Electrolyte	Temperature Coefficient
Acids	0.0164
Bases	0.0190
Salts	0.0220

Kohlrausch<sup>1</sup> showed that the curves expressing the relation between the temperature and the equivalent conductance of very dilute solutions will, if produced, cut the temperature axis at about  $-38.5^\circ$ , a point which might be called the "conductance zero." On the other hand, Bousfield and Lowry<sup>2</sup> concluded that there is no such sharply defined limit to the conductance, but that the temperature-equivalent conductance curves approach the temperature axis asymptotically. This conclusion is substantiated by the results of Kunz,<sup>3</sup> who found, for solutions of sulphuric acid, calcium chloride, and sodium hydroxide, that, instead of converging to one point, the temperature-conductance curves approached the temperature axis more and more slowly as the temperature fell, and that they would cut it probably only at absolute zero, provided that crystallization did not occur previously. Just as at low temperatures there is a conductance zero intimately connected with the viscosity of the solvent, so at high temperatures we should expect a conductance zero which depends on the increase in ion association with rising temperature.

In view of what has been said, the temperature-conductance curve should exhibit a maximum and have a point of inflection on either side of this maximum. Measurements by Sack<sup>4</sup> of the equivalent conductance of aqueous solutions of copper sulphate, over a temperature range extending up to  $120^\circ$ , showed that the equivalent conductance of 0.327, 0.5, and 0.64 per cent solutions passed through a maximum at  $94^\circ$ ,  $95^\circ$ ,

<sup>1</sup> *Sitzb. Akad. Wiss., Berlin*, **42**, 1026 (1901).

<sup>2</sup> *Proc. Roy. Soc.*, **71**, 42 (1902).

<sup>3</sup> *Z. physik. Chem.*, **42**, 591 (1903).

<sup>4</sup> *Ann. phys. Chem.*, **43**, 212 (1891).



and 96°, respectively; and measurements by Bousfield and Lowry<sup>1</sup> demonstrated the existence of points of inflection in the temperature-conductance curves for solutions of several alkali hydroxides at about 25°. For aqueous solutions of strong binary electrolytes, the maxima

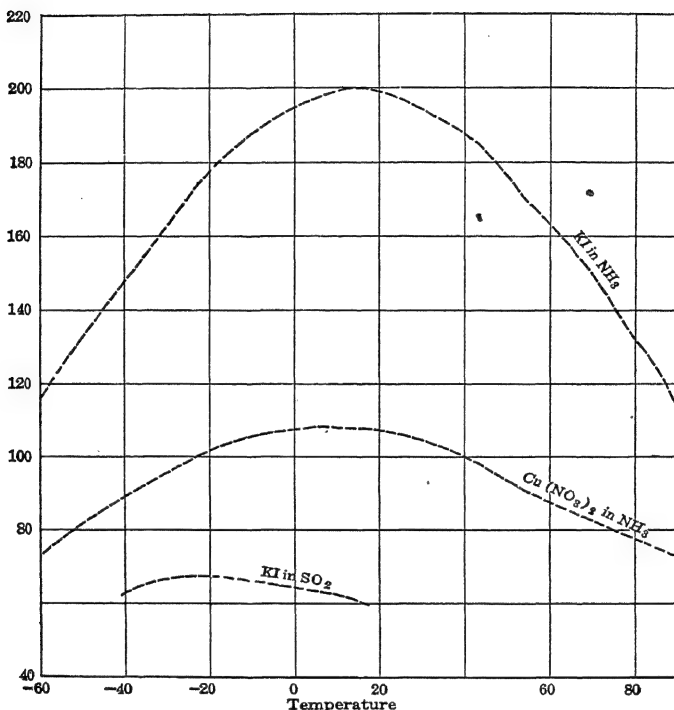


FIG. 37.

usually lie at much higher temperatures, which are lower the higher the concentration and the type of the salt. The maxima of salts of a higher type are more pronounced than those of salts of a lower type. Maxima also occur in the temperature-conductance curves of non-aqueous solutions.<sup>2</sup> In these solutions, however, the curves differ somewhat from those for aqueous solutions. In very dilute and very concentrated solu-

<sup>1</sup> *Loc. cit.*

<sup>2</sup> Cf. Franklin and Kraus, *Am. Chem. J.*, **24**, 83 (1900); Franklin, *J. Phys. Chem.*, **15**, 675 (1911); Fitzgerald, *ibid.*, **16**, 621 (1912); Blokker, *Rec. trav. chim.*, **54**, 975 (1935).

tions (normal and above), the temperature coefficient is positive; it is only at certain intermediate concentrations that the temperature coefficient changes from positive to negative as the temperature rises. The form of the temperature-conductance curve of a number of solutions is shown in Fig. 37.

The equivalent conductance of a number of molten salts has been determined<sup>1</sup> over a wide temperature interval. The results of these measurements have been reduced to the following general formulas, by means of which the value of the equivalent conductance can be calculated for any temperature included in the range given in brackets:

KNO <sub>3</sub> (346.1–500.4),	$\Lambda_t = 36.21 + 0.1875 (t - 350)$
NaNO <sub>3</sub> (321.5–487.3),	$\Lambda_t = 41.56 + 0.205 (t - 300)$
LiNO <sub>3</sub> (272.0–440.6),	$\Lambda_t = 41.14 - 0.238 (t - 300)$
RbNO <sub>3</sub> (318.8–493),	$\Lambda_t = 33.51 + 0.145 (t - 300)$
CsNO <sub>3</sub> (446.6–556.3),	$\Lambda_t = 42.13 + 0.120 (t - 450)$
KF (863.0–975),	$\Lambda_t = 101.8 + 0.3163 (t - 900)$
KCl (775.7–943.5),	$\Lambda_t = 115.4 + 0.2575 (t - 800)$
KBr (745.2–868.6),	$\Lambda_t = 90.09 + 0.1906 (t - 750)$
KI (691.5–814),	$\Lambda_t = 85.41 + 0.1564 (t - 700)$

**Application of Conductance Measurements.** (a) *Determination of the Basicity of Acids.* In his investigation of the conductance of the sodium salts of organic acids, Ostwald<sup>2</sup> found that the values of the equivalent conductance depend upon the basicity of the acid, and that the difference  $\Lambda_{1024} - \Lambda_{32}$  for solutions of such salts is approximately  $B \times 10$ , where  $B$  represents the basicity of the acid and the subscripts denote the volumes (in liters) of solution containing one equivalent of salt. Some of Ostwald's results are given in Table XXVIII.

It is evident from the results given in Table XXVIII that conductance measurements afford an excellent means of determining the basicity of an organic acid. In order to make this determination, as much sodium hydroxide (free from carbonate) solution is placed in a measuring flask as will give a  $\frac{1}{32}$  normal solution, when the flask is filled to the mark. Into this flask is run a solution of the acid under investigation, until the hydroxide is exactly neutralized, and the flask then filled to the mark with distilled water. A portion of this solution is diluted to 1/1024 normal, and the equivalent conductance of the two solutions determined. It should be mentioned that the sodium salts of the majority of inorganic acids do not follow Ostwald's rule.

<sup>1</sup> Jaeger and Kapma, *Z. anorg. Chem.*, **113**, 27 (1920); see also Arndt and Ploetz, *Z. physik. Chem.*, **110**, 237 (1924).

<sup>2</sup> *Z. physik. Chem.*, **1**, 105 (1887); **2**, 902 (1888).

(b) *The Determination of the End Point in Titration.* Since the magnitude of the conductance of a solution depends on both the concentration and the velocity of the ions, conductance measurements may be

TABLE XXVIII  
THE BASICITY OF ACIDS

Sodium Salt	$\Delta_{32}$	$\Delta_{1024}$	$\Delta_{1024} - \Delta_{32}$
<i>Salts of Monobasic Acids</i>			
Acetate.....	73.6	84.9	$1 \times 11.3$
Propionate.....	69.4	80.4	$1 \times 11.0$
Butyrate.....	66.2	76.3	$1 \times 10.1$
Valerianate.....	64.5	75.8	$1 \times 11.3$
Trichloracetate.....	70.0	80.7	$1 \times 10.7$
Average.....			$1 \times 11.0$
<i>Salts of Dibasic Acids</i>			
Oxalate.....	93.0	115.4	$2 \times 11.2$
Glutarate.....	78.0	96.9	$2 \times 9.5$
Citraconate.....	77.7	96.6	$2 \times 9.5$
Malonate.....	84.4	105.0	$2 \times 10.3$
Quinolate.....	77.2	97.0	$2 \times 9.9$
Average.....			$2 \times 10.1$
<i>Salts of Tribasic Acids</i>			
Citrate.....	80.5	108.2	$3 \times 9.2$
Aconitate.....	81.8	109.6	$3 \times 9.3$
Pyridine-tricarboxylate ( $\text{CO}_2\text{H} = 1, 2, 3$ ).....	82.1	113.1	$3 \times 10.3$
( $\text{CO}_2\text{H} = 1, 2, 4$ ).....	82.4	111.8	$3 \times 9.8$
Methyl-pyridine-tricarboxylate.....	84.3	115.1	$3 \times 10.3$
Average.....			$3 \times 9.8$

applied to the study of processes in solution which involve ionic changes, provided that such changes produce a sufficiently marked variation in the conductance of the solution.

Let us consider the simple process of the neutralization of a strong acid by a strong base. On the gradual addition of a solution of the base

to a solution of the acid, the fast-moving hydrogen ions are replaced by the slower-moving cations of the base. Therefore, since the acid and the salt which is formed are practically completely dissociated, the conductance of the solution containing the acid will gradually decrease until all the hydrogen ions disappear, i.e., until the end point is reached. If, after the end point is reached, still more of the base is added, the conductance will again increase, on account of an increase in the total number of ions present and the high velocity of the hydroxyl ions. If the

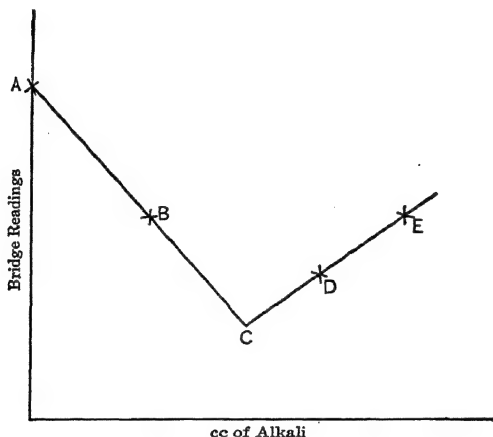


FIG. 38.

change in conductance, represented by the bridge readings when the resistance,  $R$  (Fig. 21), is kept constant, is plotted against the volume of standardized alkali added to the solution containing the acid, a curve will be obtained which resembles that given in Fig. 38. In this figure,  $C$  represents the end point of neutralization. In order to obtain the end point, it is necessary to make only four bridge readings, corresponding to the points  $A$ ,  $B$ ,  $D$ , and  $E$ , before and after the end point has been reached. The point of intersection,  $C$ , of lines drawn through the two sets of points corresponds to the end point.

In order that the points lie on two straight lines which intersect at the end point, it is necessary that the volume change during titration be kept small. This change may be minimized by having the titrant 10–20 times as concentrated as the solution being titrated. However, a correction must be applied for accurate work.<sup>1</sup> The more acutely the con-

<sup>1</sup> Righellato and Davies, *Trans. Faraday Soc.*, **29**, 429 (1933).

ductance lines cut one another, the greater the precision in estimating the end point. This may be achieved by the proper choice of titrants.<sup>1</sup> When other electrolytes are absent, fair accuracy may be obtained in the titration of solutions as dilute as 0.0001 normal.<sup>2</sup>

The conductance method may also be employed to titrate a strong acid in the presence of a weak acid. The conductance changes which take place when a standardized solution of sodium hydroxide is added to a solution containing equivalent quantities of, say, hydrochloric acid and acetic acid are represented in Fig. 39. It will be observed that the

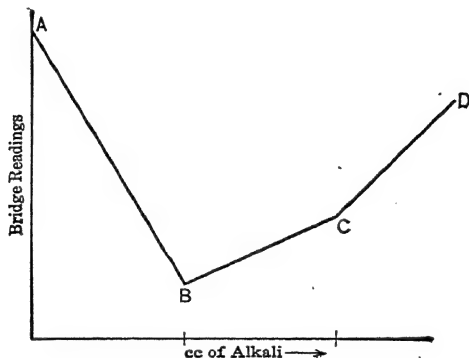


FIG. 39.

conductance decreases rapidly along  $AB$ , until all the hydrochloric acid is neutralized.<sup>3</sup> This decrease is followed by a rise in conductance along  $BC$ , in consequence of the replacement of the slightly dissociated acetic acid by its completely dissociated salt. After the acetic acid has been neutralized, further addition of sodium hydroxide produces a more marked increase in the conductance (along  $CD$ ), due to the accumulation of sodium and fast-moving hydroxyl ions in the solution. In Fig. 39 the points  $B$  and  $C$  correspond to the end points of the neutralization of the hydrochloric acid and the acetic acid, respectively.

The conductance method is particularly useful in determining the end point in colored or turbid solutions, in which the color of an indicator would be more or less concealed. Conductometric titrations may also be employed to follow many reactions involving the formation of

<sup>1</sup> Cf. Eastman, *J. Am. Chem. Soc.*, **47**, 332 (1925).

<sup>2</sup> Cf. Jander and Schorstein, *Z. angew. Chem.*, **45**, 701 (1932).

<sup>3</sup> When a solution of a base is added to a solution containing two acids of markedly different strengths, practically all the stronger acid will be neutralized before the base combines with the weaker acid. Cf. Chapter XX.

weak electrolytes or sparingly soluble products.<sup>1</sup> Because of the design of special cells<sup>2</sup> and simplification of procedure, these methods should find increasing application in analytical work. Among the many processes studied during recent years there may be mentioned the titration of: acids and bases of different concentrations, and mixtures of acids;<sup>3</sup> mixtures of sodium hydroxide and sodium carbonate;<sup>4</sup> phenols;<sup>5</sup> fatty acids;<sup>6</sup> zinc chloride and cyanates;<sup>7</sup> sodium molybdate and sodium tungstate;<sup>8</sup> anions yielding slightly soluble salts of barium, lead, mercury; or silver.<sup>9</sup> In precipitation reactions, the chief sources of error are (a) solubility of the precipitate, (b) its rate of formation, and (c) the uncertainty of its composition. The first two of these sources of error may sometimes be eliminated by the addition of alcohol;<sup>10</sup> the last by titrating in hot solution.<sup>11</sup>

Conductance measurements have been applied to the concentration control of solutions.<sup>12</sup>

#### REFERENCES

- KRAUS, *The Properties of Electrically Conducting Systems*, Chapters V and VI, 1922.  
WALDEN, *Salts, Acids and Bases*, Chapter VIII, 1929.

#### PROBLEMS

1. Calculate the specific conductance of mercury at 0°.

2. In measuring the conductance of succinic acid, it was found that with a  $\frac{1}{100}$ -molar solution there was a minimum in the telephone when  $x = 34.65$  cm and  $R = 500$  ohms. The cell constant was obtained from the following data: with a 0.1 normal solution of potassium chloride, at 25°, a position of minimum sound was obtained at  $x = 64.69$  when  $R = 50$  ohms. Calculate the molar conductance of succinic acid at the above concentration.

3. Calculate the equivalent conductance at zero concentration of acetic acid, being given that at 18° the  $\Lambda_0$  values of hydrochloric acid, potassium chloride, and potassium acetate are 380.0, 130.0, and 100.0, respectively.

<sup>1</sup> Cf. Kolthoff, *Ind. Eng. Chem., Anal. Ed.*, **2**, 225 (1930).

<sup>2</sup> Britton and German, *J. Chem. Soc.*, **1930**, 1249; Preston, *ibid.*, **1931**, 1827.

<sup>3</sup> Righellato and Davies, *Trans. Faraday Soc.*, **29**, 437 (1933).

<sup>4</sup> Auméras and Marcon, *Bull. Soc. chim.* [iv], **61**, 1594 (1932).

<sup>5</sup> Pfundt and Junge, *Ber.*, **62**, 515 (1929).

<sup>6</sup> Jander and Weitendorf, *Z. angew. Chem.*, **45**, 705 (1932).

<sup>7</sup> Pfundt, *ibid.*, **46**, 218 (1933).

<sup>8</sup> Rother and Jander, *ibid.*, **43**, 930 (1930).

<sup>9</sup> Jander, Pfundt, and Schorstein, *ibid.*, **43**, 507 (1930); Kolthoff and Kameda, *Ind. Eng. Chem., Anal. Ed.*, **3**, 129 (1931); Pfundt, *Z. angew. Chem.*, **46**, 200 (1933).

<sup>10</sup> Kolthoff, *Z. anal. Chem.*, **61**, 171 (1922).

<sup>11</sup> Harned, *J. Am. Chem. Soc.*, **39**, 252 (1917).

<sup>12</sup> For a review of this application, see Belen'kil, *Zavodskaya Lab.*, **10**, 349 (1941).

4. The conductances of 0.00001 normal (zero concentration) solutions of salts have been determined at  $18^\circ$ , using a resistance of 10,000 ohms and a conductance cell having a constant  $K = 0.0362$ . With solutions of potassium chloride, sodium nitrate, and sodium chloride, the position of minimum sound was 26.42 cm, 22.53 cm, and 23.14 cm, respectively. From these data calculate the equivalent conductance at zero concentration of potassium nitrate.

5. The equivalent conductance of potassium iodate is 74.34, 79.67, 84.06, 91.24, and 96.04, respectively, at concentrations of 0.2, 0.1, 0.05, 0.01, and 0.001 normal. Given that the specific conductances of potassium chloride, sodium iodate, and sodium chloride are, respectively, 0.000001301, 0.000000774, and 0.00000109, at a dilution of 100,000 liters, calculate the conductance ratio of potassium iodate at the above concentrations.

6. Given that the conductance ratio of 0.01 normal thallium chloride is 0.915 at  $18^\circ$ , and that its equivalent conductance at zero concentration is 131.4, calculate the specific conductance of the salt at a dilution of 100 liters.

7. With a  $\frac{1}{32}$  normal solution of the sodium salt of nicotinic acid the position of minimum sound was 51.18, when  $R = 50$  ohms; with a  $1/1024$  normal solution of the salt the position of minimum sound was 43.00, when  $R = 1000$  ohms. Given that the cell constant was 0.102, calculate the basicity of nicotinic acid.

8. Ten cubic centimeters of a solution of sodium hydroxide was placed in a conductance cell, which was then balanced against a resistance  $R$ . A solution of 0.1 normal hydrochloric acid was added to the cell from a burette, a few cubic centimeters at a time, and the position of minimum sound determined after each addition of acid, the resistance  $R$  remaining unchanged. From the following data, calculate the normality of the sodium hydroxide solution:

Burette reading	0.00	2.00	8.00	11.00	13.00 cc
Bridge wire reading	50.8	44.0	25.6	23.9	31.0 cm

9. Parallel electrodes having an area of  $5 \text{ cm}^2$  and separated by a distance of 10 cm are placed in a solution of 0.01 normal acetic acid at  $18^\circ$ . On the application of a potential difference of 70 volts to the electrodes, a current of 0.005 ampere flows through the solution. Calculate the specific and equivalent conductances of acetic acid.

10. At  $18^\circ$  the equivalent conductance of  $\text{KClO}_3$  has the following values:

$\Lambda$	99.1	112.6	114.7	117.8	118.7	120.2
$c$	0.1	0.01	0.005	0.001	0.0005	0.0001

From these data determine  $\Lambda_0$  for  $\text{KClO}_3$  by plotting  $1/\Lambda$  against  $\sqrt{\Lambda c}$  and extrapolating the best straight line through the points.

## CHAPTER VI

### THE MIGRATION OF IONS

**The Transport of Electricity by the Ions.** We have seen in the preceding chapter that the conductance of an electrolyte depends upon the velocities as well as upon the concentration of its ions. We shall now ascertain to what extent each ion shares in the carrying of the current. It is evident that the current is equally divided between the ions of a binary electrolyte only when they travel at the same velocity. The part played by each ion in the transport of electricity through a solution was first studied by Hittorf,<sup>1</sup> in his classical researches on the concentration changes which occur in the neighborhood of the electrodes during electrolysis. A moment's reflection will make it clear that these changes in ion concentration must be a measure of the velocities of the ions, for, the greater the velocity of an ion, the greater will be the change in the concentration of the ion in the vicinity of the electrode from which it moves away. It must be remembered, however, that, although the ions may—and usually do—move through a solution at different velocities, *equivalent quantities of each ion always separate at the anode and the cathode*, in accordance with Faraday's second law of electrolysis. Thus, for every 96,500 coulombs of electricity which pass through a solution of an electrolyte, one equivalent of anion is liberated at the anode and one equivalent of cation is set free at the cathode, regardless of the velocities of the ions.

In order to gain a clearer idea of how a quantity of electricity which passes through a solution is divided between the ions, let us first consider the electrolysis of a solution of a uniunivalent electrolyte, MA, between insoluble electrodes, and let us assume that the ions,  $M^+$  and  $A^-$ , move with *equal* velocities, i.e., that  $u = v$ . Suppose that the solution, containing, say, 24 equivalents of MA, is placed in an electrolytic cell (Fig. 40) divided into an anode section, a middle section, and a cathode section by imaginary partitions,  $P_1$  and  $P_2$ ; and that before the commencement of electrolysis the ions are distributed as shown in Fig. 40. If 6 faradays of electricity is now passed through the solution, 6 equivalents of the cation,  $M^+$ , will separate at the cathode,  $E_2$ , and 6 equivalents of the anion,  $A^-$ , will be set free at the anode,  $E_1$ , in accord-

<sup>1</sup> *Pogg. Ann.*, 89, 177 (1853) and later volumes of this journal; cf. Ostwald's *Klassiker exakt. Wiss.*, Nos. 21 and 23.



ance with Faraday's law. Further, since  $u = v$ , the 6 faradays of electricity will be equally divided between the two kinds of ions and,

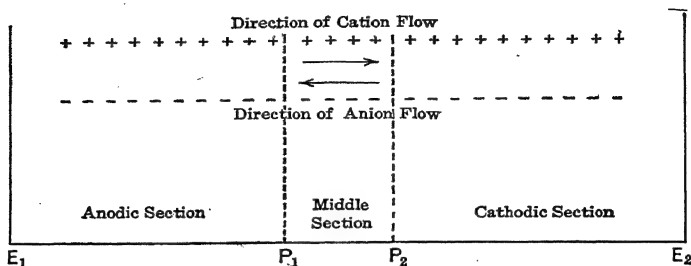


FIG. 40.

therefore, 3 equivalents of  $M^+$  will move into the cathode section, and 3 equivalents of  $A^-$  will pass into the anode section. After the passage of the 6 faradays, the ions will be distributed as shown in Fig. 41.

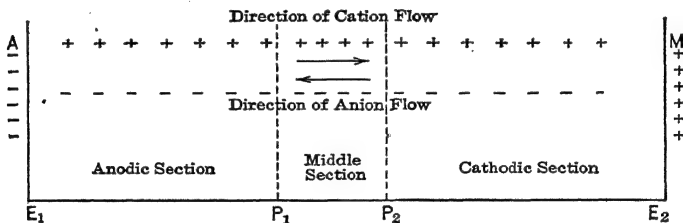


FIG. 41.

**The Concentration Changes in the Vicinity of the Electrodes.** From Figs. 40 and 41, it will be observed that changes in concentration in the neighborhood of the electrodes result from reductions by separation, from reductions by migration, and from increases by migration. The changes in concentration which occurred in the three sections during electrolysis, in the case discussed above, may be summarized as follows:

	Anode Section. Equivalents of:		Middle Section. Equivalents of:		Cathode Section. Equivalents of:	
	$M^+$	$A^-$	$M^+$	$A^-$	$M^+$	$A^-$
Reduction by separation...	0	6	0	0	6	0
Reduction by migration...	3	0	3	3	0	3
Increase by migration.....	0	3	3	3	3	0
Total reduction.....	3	3	0	0	3	3
Final concentration of MA.	7		4		7	

Since different ions usually move at different velocities, let us now consider the electrolysis of a uniunivalent electrolyte, MA, which yields ions having different velocities. For example, suppose that the velocity of the cation is five times that of the anion, which would represent, approximately, the difference in the velocities of the ions of hydrochloric, hydrobromic, hydriodic, or nitric acid. As before, suppose that the solution contains 24 equivalents of MA (distributed as in Fig. 40). If 6 faradays of electricity is passed through this solution, 6 equivalents of  $M^+$  will separate at the cathode and the same number of  $A^-$  will be set free at the anode. Since, then,  $u = 5v$ , the 6 faradays of electricity will be

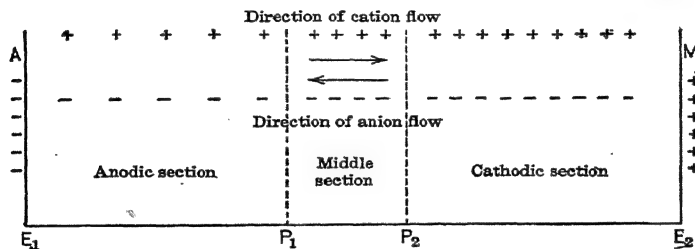


FIG. 42.

divided between the cations and anions in the ratio of 5 to 1. Hence, 5 equivalents of  $M^+$  will move into the cathode section and one equivalent of  $A^-$  will enter the anode section, during the passage of the current. At the conclusion of electrolysis, the ions will be distributed as shown in Fig. 42. The concentration changes which occurred in the three sections may be summarized as follows:

	Anode Section. Equivalents of:		Middle Section. Equivalents of:		Cathode Section. Equivalents of:	
	$M^+$	$A^-$	$M^+$	$A^-$	$M^+$	$A^-$
Reduction by separation...	0	6	0	0	6	0
Reduction by migration...	5	0	5	1	0	1
Increase by migration.....	0	1	5	1	5	0
Total reduction.....	5	5	0	0	1	1
Final concentration of MA.	5		4		9	

From the foregoing it is evident that the reduction in the number of equivalents of the cation in the anode section, due to migration, is proportional to the velocity of the cation, and that the reduction in the

number of equivalents of the anion in the cathode section, due to migration, is proportional to the velocity of the anion. Hence

$$\frac{\text{Reduction in the number of equivalents of the cation in the anode section due to migration}}{\text{Reduction in the number of equivalents of the anion in the cathode section due to migration}} = \frac{u}{v} \quad (1)$$

It follows from this equation that equal reductions in the anode and cathode sections occur only when the velocities of the ions are equal.

When electrolysis takes place between insoluble electrodes, the preceding summaries of the concentration changes show that the reduction in the concentration of the anion in the cathode section, due to migration, and that of the cation in the anode section, also due to migration, are equal to the total reductions in the concentration of the electrolyte in the anode and cathode sections, respectively. In order to ascertain the reductions in concentration *due to migration*, when either of the ion constituents is dissolved off the electrodes, as happens when a solution of silver nitrate is electrolyzed between silver electrodes, the amount which dissolves must be calculated with the help of Faraday's law and deducted from the change in concentration of that ion constituent in the electrode section.

**Transference Numbers.** We have seen in the preceding chapter that the quantity of electricity transported by one equivalent of cation in 1 second is  $uF$  coulombs, and that the quantity carried by one equivalent each of cation and anion in the same time is  $(u + v)F$  coulombs. Therefore

$$\frac{u}{u + v}$$

equals the ratio of the number of coulombs transported by the cations to the number of coulombs carried by both ions. Similarly

$$\frac{v}{u + v}$$

equals the ratio of the number of coulombs transported by the anions to the number of coulombs carried by both ions. These ratios

$$\frac{u}{u + v} = n_c \quad (2)$$

and

$$\frac{v}{u + v} = n_a \quad (2a)$$

are called the **transference numbers** of the ions of an electrolyte. These numbers represent the fraction of the total current carried by each kind of ion, or *the number of equivalents of each ion constituent transferred per faraday*.

Since the transference number depends upon the velocities of both ions, obviously the value of the transference number of a given ion must vary with the electrolyte from which the ion is derived. Accordingly, when solutions of, say, potassium chloride and lithium chloride are electrolyzed, the fraction of the current carried by the chlorine ion is not the same in the two cases.

As shown in Figs. 40, 41, and 42, the sum of the reductions (due to migration) in the number of equivalents of the cation and the anion in the anode and cathode sections, respectively, is equal to the number of faradays that pass through a solution of an electrolyte. When, therefore, a coulometer is placed in series with the electrolytic cell, equations 2 and 2a may be written:

$$n_c = \frac{u}{u + v}$$

$$= \frac{\text{Reduc. in no. of equiv. of cation in anode sec. due to migration}}{\text{Number of equivalents of metal deposited in coulometer}} \quad (3)$$

and

$$n_a = \frac{v}{u + v}$$

$$= \frac{\text{Reduc. in no. of equiv. of anion in cathode sec. due to migration}}{\text{Number of equivalents of metal deposited in coulometer}} \quad (3a)$$

**Determination of Transference Numbers.**<sup>1</sup> In order to determine the transference numbers of the ions of an electrolyte, it is simply necessary to remove portions of the solution from the immediate neighborhood of the electrodes, and to determine the changes in concentration due to the passage of a known quantity of electricity. *The success of the determination depends upon interrupting electrolysis before any alteration in the concentration of the solution in the middle section takes place.* This method was first employed by Hittorf. In order to show its simplicity, the determination of the transference number of the ions of silver nitrate is here described.

<sup>1</sup> An excellent bibliography and criticism of all transference work published up to the end of 1905 is given in a paper by McBain, *Proc. Wash. Acad. Sci.*, **9**, 1 (1907); and a summary covering work to the end of 1938 appears in a paper by Le Roy, *Univ. Toronto Studies, Papers Chem. Labs.*, No. 156 (1939).

A solution of silver nitrate is electrolyzed in a cell (Fig. 43) designed to prevent convection currents which, if they occurred, would vitiate the results.

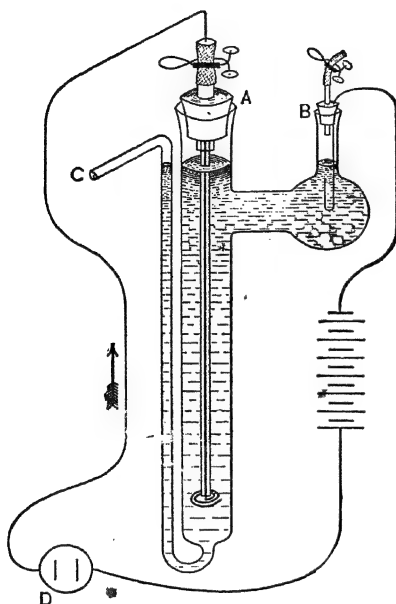


FIG. 43.

In this cell the cathode, *B*, consists of a piece of cylindrical silver foil and the anode, *A*, is made of heavy silver wire bent in the form of a spiral. The vertical portion of this wire is separated from the solution by a covering of glass tubing. During the experiment, the electrolysis cell is placed in series with a coulometer, *D*, and a feeble current passed through the solution.<sup>1</sup> At the conclusion of the experiment, about one-third of the solution (anode solution) is removed at *C* into a weighed bottle. A second portion of the solution (middle solution) is then run off into another weighed bottle. These two portions of the solution are weighed and their silver content determined by analysis. The second portion of solution serves to show whether the concentration of the middle section has undergone any change during electrolysis.

Various other forms of apparatus for the determination of transference numbers have been constructed. The H-shaped vessels designed by Findlay<sup>2</sup> and by Getman<sup>3</sup> are very satisfactory. With Findlay's apparatus (Fig. 44), the middle portion of the solution is easily separated at the end of the experiment. This consists of three tubes, *A*, *B*, and *C*, all of which are furnished with stopcocks through which the solution can be run out. The two outer tubes are connected to the U-tube

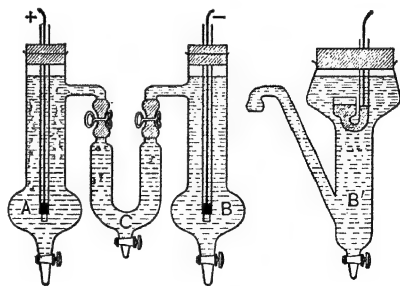


FIG. 44.

<sup>1</sup> The use of a micro-coulometer has been suggested by Reevly and Gordon, *Trans. Electrochem. Soc.*, **63**, 167 (1933).

<sup>2</sup> *Chem. News*, **100**, 185 (1909).

<sup>3</sup> *J. Am. Chem. Soc.*, **36**, 1640 (1914).

by means of rubber tubing furnished with spring clips. During an experiment the clips are kept open, but at the end of the period of electrolysis they are closed, and the solution for analysis is run through the stopcock at the bottom of the appropriate outer tube into a weighed flask. This tube and the electrode are washed with a small quantity of the original solution, the washings being collected in the same weighed flask. The solution in the U-tube, representing the middle section, is then run into a second weighed flask. In experiments in which gas is developed at the cathode, the tube *B* is replaced by a tube, *B'*, carrying a mercury cathode. This apparatus is simple to use and may be employed with all solutions.

**The Calculation of Transference Numbers.** In an actual determination of the transference numbers of the ions in silver nitrate, in which a 0.6819 per cent solution of the salt was electrolyzed between silver electrodes, in a cell placed in series with a copper coulometer, the following data were obtained: After electrolysis the anode solution, weighing 27.67 grams, was found to contain 0.2326 gram of silver nitrate; the middle portion, weighing 19.48 grams, was found to contain 0.1326 gram of silver nitrate; and it was found that 0.0160 gram of copper had been deposited in the coulometer.

Since 99.32 grams of water are associated with 0.6819 gram of silver nitrate in the original solution, it is evident that 19.35 grams of water (the weight of water contained in the middle portion withdrawn from the cell after electrolysis) contains 0.1326 gram of silver nitrate. Hence, the concentration of the middle portion did not change during electrolysis.

In the anode solution, 27.44 grams of water are associated with 0.2326 gram of silver nitrate or with 0.001372 equivalent of silver. If the concentration of this solution had undergone no change during electrolysis, 27.44 grams of water would have been associated with 0.1884 gram of silver nitrate or 0.001109 equivalent of silver. Therefore, the anode solution has gained  $0.001372 - 0.001109 = 0.000263$  equivalent of silver. Since 0.0160 gram or 0.000503 equivalent of copper was deposited in the coulometer, 0.000503 equivalent of silver must have dissolved from the anode of the electrolytic cell and passed into the anode solution. Hence, if no silver ions had migrated from the anode section, there ought to have been an increase of 0.000503 equivalent of silver in the anode solution. Since, however, the increase is only 0.000263 equivalent,  $0.000503 - 0.000263 = 0.000240$  equivalent of silver must have migrated from the anode section towards the cathode. Therefore, from equation 3,

$$n_c = \frac{0.000240}{0.000503} = 0.477$$

Whence it follows that the transference number of the anion ( $\text{NO}_3^-$ ) is

$$n_a = \frac{v}{u+v} = 1 - \frac{u}{u+v} = 1 - 0.477 = 0.523$$

**The Transference Numbers of the Ions of Polyionic Electrolytes.** So far we have considered only the transference numbers of binary electrolytes. We shall now obtain an expression for the transference number of an ion of an electrolyte which yields more than two ions. If we represent the equivalent decrease (due to migration) of the cation in the anode section and that of the anion in the cathode section by  $N_M$  and  $N_A$ , respectively, equations 3 and 3a may be written

$$n_c = \frac{N_M}{N_M + N_A} \quad (4)$$

and

$$n_a = \frac{N_A}{N_M + N_A} \quad (4a)$$

We may state, then, that the transference number of the cation (or anion) of an electrolyte is equal to the ratio of its equivalent decrease in the anode (or cathode) section to the arithmetical sum of the total equivalent decrease of the cations in the anode section and that of the anions in the cathode section. Thus, for an electrolyte whose positive ions are  $M'$ ,  $M''$ ,  $\dots$ , and whose negative ions are  $A'$ ,  $A''$ ,  $\dots$ , the transference number of the cation,  $M'$ , is given by the expression

$$n_{M'} = \frac{N_{M'}}{(N_{M'} + N_{M''} + \dots) + (N_{A'} + N_{A''} + \dots)} \quad (5)$$

The transference numbers of the cations of a number of binary and ternary electrolytes, at  $18^\circ$ , are given in Table XXIX.<sup>1</sup>

TABLE XXIX

TRANSFERENCE NUMBERS OF CATIONS IN 0.02 *N* SOLUTION AT  $18^\circ$

Electrolyte	$n_c$	Electrolyte	$n_c$
NaCl	0.396	CaCl <sub>2</sub> ( $20^\circ$ )	0.424
KCl	0.496	SrCl <sub>2</sub> ( $20^\circ$ )	0.435
LiCl	0.328	CdCl <sub>2</sub>	0.430
NH <sub>4</sub> Cl	0.492	CdBr <sub>2</sub>	0.430
NaBr	0.395	CdI <sub>2</sub>	0.442
KBr	0.495	Na <sub>2</sub> SO <sub>4</sub>	0.390
AgNO <sub>3</sub>	0.471	K <sub>2</sub> SO <sub>4</sub>	0.492
HCl	0.833	H <sub>2</sub> SO <sub>4</sub>	0.822
HNO <sub>3</sub>	0.841	CuSO <sub>4</sub>	0.375
MgSO <sub>4</sub>	0.381	CdSO <sub>4</sub>	0.384

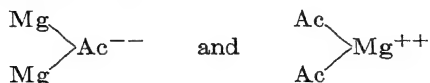
<sup>1</sup> A. A. Noyes and Falk, *J. Am. Chem. Soc.*, **33**, 1436 (1911).

**The Influence of Concentration on Transference Numbers.** Owing to hydration of the ions, variations in the values of the "Hittorf" transference numbers with concentration are to be expected. That such variations are in accord with experimental data is shown by Table XXX.<sup>1</sup>

TABLE XXX  
INFLUENCE OF CONCENTRATION ON THE TRANSFERENCE NUMBERS OF  
CATIONS AT 18°

Concentration	0.005 N	0.01 N	0.02 N	0.05 N	0.1 N	0.3 N	0.5 N
NaCl	0.396	0.396	0.396	0.395	0.393	0.388	0.382
KCl	0.496	0.496	0.496	0.496	0.495	.....	.....
LiCl	.....	0.332	0.328	0.320	0.313	0.299	.....
HCl	0.832	0.833	0.833	0.834	0.835	0.838	0.840
CdBr <sub>2</sub>	0.430	0.430	0.430	0.430	0.429	0.389	0.350
CdI <sub>2</sub>	0.445	0.444	0.442	0.396	0.296	0.046	0.003
CdSO <sub>4</sub>	.....	0.389	0.384	0.374	0.364	0.340	0.323
CuSO <sub>4</sub>	.....	.....	0.375	0.375	0.373	0.348	0.327

It will be observed from the values given in the table that the transference numbers of the ions of uniunivalent electrolytes change but slightly with concentration, even at higher concentrations, and remain constant at concentrations below 0.02 normal. The small changes observed are doubtless due to hydration. On the other hand, the much greater variations in the values of the transference numbers of the ions of ternary electrolytes cannot be ascribed to this influence. These changes are probably due to the presence, at higher concentrations, of complex or intermediate ions possessing quite different velocities from those of the simple ions of the electrolyte. Further, the nature of these ions may be such that they carry some of the simple anion and cation to the cathode and anode, respectively, during electrolysis. With decreasing concentration, these ions dissociate into their simple constituents, and probably disappear entirely when the solution becomes very dilute. The existence of complex and intermediate ions in solutions of electrolytes of higher types has been demonstrated by a number of investigators.<sup>2</sup> For example, Bredig showed that at higher concentrations a solution of magnesium acetate contained the ions



<sup>1</sup> A. A. Noyes and Falk, *J. Am. Chem. Soc.*, **33**, 1436 (1911).

<sup>2</sup> Cf. Bredig, *Z. physik. Chem.*, **13**, 202 (1894); A. A. Noyes, *J. Am. Chem. Soc.*, **23**, 54 (1901); Drucker, *Z. Elektrochem.*, **19**, 797 (1913); Harkins and Pearce, *J. Am. Chem. Soc.*, **38**, 2679 (1916); Dole, *Trans. Electrochem. Soc.*, **77**, 385 (1940).



which migrated towards the anode and cathode, respectively; and Heym<sup>1</sup> attributed the very marked decrease, with dilution, in the value of the transference number of the iodine ion in cadmium iodide (see Table XXX) to the disappearance of the complex ion,  $(I_2Cd \cdot I_2)^{--}$ , present at higher concentrations.

**The Influence of Temperature on Transference Numbers.** As might be expected, the transference numbers of ions change with temperature. It has been observed that transference numbers below 0.5 increase and those above 0.5 decrease as the temperature increases, thus showing that the velocity and the transference of the different ion constituents vary by a small fractional amount at higher temperatures. This behavior, which is illustrated by the values of  $n_c$  in Table XXXI,<sup>2</sup> may be

TABLE XXXI

INFLUENCE OF TEMPERATURE ON TRANSFERENCE NUMBERS IN 0.02  
NORMAL SOLUTION

Temperature	0°	18°	30°	96°
NaCl	0.387	0.396	0.404	0.442
KCl	0.493	0.496	0.498	( $c = 0.05 N$ )
NH <sub>4</sub> Cl	0.489	0.492	0.495	
HCl	0.844	0.833	0.822	0.748
AgNO <sub>3</sub>	0.461	0.471	0.481	( $c = 0.01 N$ )

attributed to a greater degree of hydration of the slower-moving ion, and to a decrease in the degree of hydration with rise in temperature.

**The Moving-Boundary Method for the Determination of Transference Numbers.** The determination of transference numbers by the "Hittorf" method is essentially equivalent to determining the relative quantities of the various ion constituents which pass a given cross section of solution in either direction. The position of this imaginary cross section is such that the quantity of solvent between it and the electrode remains unchanged during electrolysis. Since the number of equivalents ( $N$ ) of any ion which passes through this cross section, in a given time, is proportional to the concentration ( $C$ ) of the ion and its velocity, then, as is evident from equation 5, the transference number of the cation,  $M'$ , of any electrolyte is given by the expression:

$$n_c = \frac{u_{M'}C_{M'}}{(u_{M'}C_{M'} + u_{M''}C_{M''} + \dots) + (v_{A'}C_{A'} + v_{A''}C_{A''} + \dots)} \quad (6)$$

For binary electrolytes, this expression reduces to equation 2.

<sup>1</sup> *Ann. Physik.*, **12**, 443 (1919).

<sup>2</sup> A. A. Noyes and Falk, *J. Am. Chem. Soc.*, **33**, 1436 (1911).

In the Hittorf method, the relative velocities of the ions are determined indirectly. In the moving-boundary method, developed and employed by Denison and Steele,<sup>1</sup> the velocities of the ions of an electrolyte are determined by measuring the distance traveled by the boundaries of a solution of the electrolyte, when placed between solutions of two other salts which serve as indicators, i.e., which produce a boundary with the middle solution. The transference number of one of the two ions of the electrolyte is equal to the distance moved by the boundary of that ion constituent divided by the sum of the distances moved in the same time and under the same potential gradient by the boundaries of both ion constituents. In order that the boundaries remain well defined and sharp during electrolysis, it is necessary for one of the two solutions to have the same anion as the middle solution, but a materially slower cation, and for the second solution to have the same cation as the middle solution, and a materially slower anion. In the determination of the transference numbers of the ions of potassium chloride by this method, Steele placed the solution of this salt between solutions of lithium chloride and potassium acetate, and passed the current from the lithium chloride to the potassium acetate. During electrolysis, the boundary lines are quite visible on account of the different refractive indices of the solutions. Any tendency for a boundary line to become diffuse and hazy on account of diffusion and convection is offset by a restoring effect, which depends on the unequal potential gradients in the two solutions during the passage of the current. By way of illustration of this effect, consider the boundary line between the lithium chloride and potassium chloride solutions referred to above. Any relatively fast-moving potassium ions that diffuse or are carried by convection across this boundary into the region of higher potential gradient existing in the lithium chloride solution have their velocity increased and thus catch up with the moving boundary; while, conversely, relatively slow-moving lithium ions that cross the boundary into the region of lower potential gradient existing in the potassium chloride solution have their speed reduced, thus permitting the moving boundary to catch up with them.<sup>2</sup>

MacInnes and his co-workers<sup>3</sup> have developed a modification of the

<sup>1</sup> *Z. physik. Chem.*, **57**, 110 (1906); cf. Steele, *ibid.*, **40**, 689 (1902); Denison, *Trans. Faraday Soc.*, **5**, 165 (1909).

<sup>2</sup> Cf. MacInnes and Longworth, *Chem. Revs.*, **11**, 194 (1932). For a theory of the moving-boundary method, see Hartley, *Proc. Roy. Soc.*, **A140**, 141 (1933).

<sup>3</sup> MacInnes and Smith, *J. Am. Chem. Soc.*, **45**, 2246 (1923); **46**, 1398 (1924); **47**, 1009 (1925). MacInnes and Cowperthwaite, *ibid.*, **48**, 1909 (1926); **49**, 1707 (1927); **51**, 2671 (1929). Longworth and MacInnes, *J. Optical Soc. Am. and Rev. Sci. Inst.*, **19**, 50 (1929). Longworth, *J. Am. Chem. Soc.*, **54**, 2741 (1932). For an excellent review of the moving-boundary method and bibliography, see MacInnes and Longworth, *Chem. Revs.*, **11**, 171-230 (1932).

moving-boundary method, involving a single boundary. This depends upon measuring, with a silver coulometer, the quantity of current which passes through the circuit during the time required for a single boundary to sweep through a known volume. Since, during the passage of 1 faraday,  $F$ , of electricity through the solution, a single boundary sweeps through a volume  $n\phi$  (where  $\phi$  is the volume of solution which contains one equivalent), the volume traversed by the boundary during the passage of  $Q$  coulombs will be

$$V = \frac{n\phi Q}{F} \quad (7)$$

Accordingly, the transference number is

$$n = \frac{VF}{\phi Q} \quad (8)$$

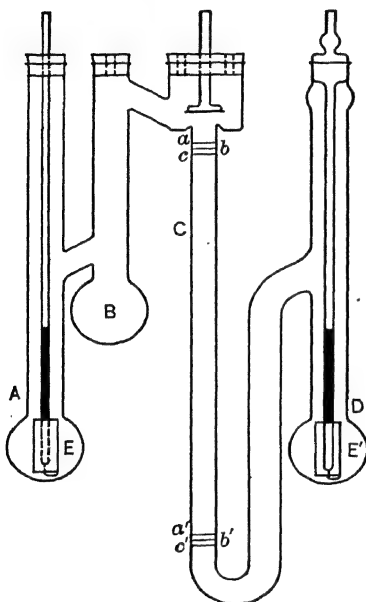


FIG. 45.

One of the forms of apparatus employed by MacInnes and Smith is shown in Fig. 45. In this the electrode tubes  $A$  and  $D$  are far enough removed from the measuring tube,  $C$ , so that concentration changes taking place in the former cannot alter the concentration of the solution in  $C$ . The electrodes,  $E$  and  $E'$ , are made of platinum gauze, coated electrolytically with silver, the cathode,  $E'$ , being also coated with silver chloride by electro-

lysis. The electrodes are made in the form of a cylinder which surrounds the lower end of the glass tube, as shown in the figure. The measuring tube,  $C$ , having an internal diameter of 1.1 centimeters, is calibrated with mercury for three volumes between the marks  $a$  and  $a'$ ,  $b$  and  $b'$ , and  $c$  and  $c'$ , which are etched completely round the tube to eliminate errors due to parallax. The tubes  $D$  and  $C$  are filled with the solution of the electrolyte under investigation, which is kept out of the tubes  $B$  and  $A$ . The tube  $D$  is then closed with the combination ground-glass stopper and electrode, and any excess of the solution is squeezed into the enlarged portion of  $C$  by means of the circular rubber disk indicated in the figure. This excess solution is removed by means of a pipette thrust through one of the openings in the rubber stopper holding the glass rod which carries the rubber disk. The bulb

of tube *A* is filled with a 0.5 normal solution of the indicator (e.g., lithium chloride), the anode *E* is put firmly in place, and the tube *B* and the remainder of *A* are filled through an opening in the stopper closing *B* with a less concentrated solution of the indicator. The rubber disk is gently loosened, but not pulled up, so that several milliamperes pass through the circuit. The boundary between the solutions immediately starts down the tube, and after it has advanced a short distance the rubber disk is carefully pulled up. As the boundary passes each mark on the upper part of tube *C*, a coulometer is thrown in the circuit and allowed to remain in the circuit until the boundary reaches the corresponding mark on the lower part of *C*.

Although highly accurate results have been obtained with the apparatus just described, as well as with the original apparatus of Denison and Steele, very skillful and delicate manipulation is required. One of the difficulties is bringing together the solutions in such a way as to form sharp boundaries. This difficulty has been ingeniously overcome by MacInnes and Brighton<sup>1</sup> in a further modification of the moving-boundary apparatus. This new form of apparatus, which requires no special skill to operate, they describe as follows: "The electrode vessel *A*

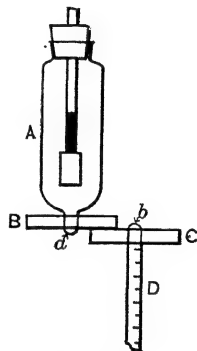


FIG. 46.

(Fig. 46) is fitted into the disc *B*, and the graduated tube *D* into the corresponding disc *C*, the discs *B* and *C* both having plane surfaces.<sup>2</sup> The electrode vessel *A* is filled with the indicator solution and is closed with a stopper which carries the electrode. A drop of the solution *a* hangs from the open end of the electrode tube. (The filling can be accomplished by holding a finger over the opening until the stopper is in place, and a tighter seating of the stopper then forms the pendant drop.) The graduated tube *D* is filled with a slight excess of [the electrolyte] solution so that a drop *b* protrudes. Now if the disc *B* is slid over the disc *C* the excess of both solutions will be sheared away and a sharp boundary will result when the tubes are in place over each other. If the solutions are properly selected and a current of electricity caused to flow, the boundary will travel down the graduated tube *D*." (The adjacent surfaces of the disks are coated with a thin layer of vaseline.) From the volume swept through by the boundary, the transference number can

<sup>1</sup> *J. Am. Chem. Soc.*, **47**, 994 (1925).

<sup>2</sup> For a description and illustration of a form of disk which overcomes the errors due to electrical leaks and which increases the ease of manipulation, see MacInnes and Brighton, *ibid.*, **47**, 997 (1925).

be calculated by means of equation 8. If, as frequently happens, the number of coulombs is too small to be measured accurately with a coulometer, the quantity of electricity can be calculated from the product  $I \times t = Q$  (where  $I$  is the current strength and  $t$  is the time), provided that the current strength can be kept constant. As hand regulation of the current is not only tedious but also inaccurate, an apparatus has been devised for producing and maintaining, automatically, a constant current.<sup>1</sup>

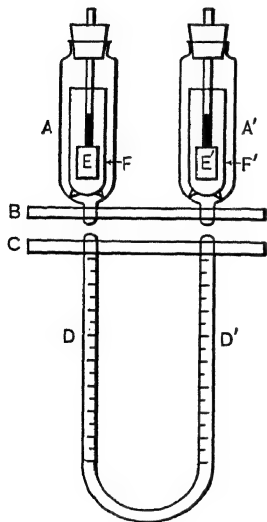


Fig. 47.

An apparatus by means of which two boundaries can be formed simultaneously is illustrated in Fig. 47. The glass cups,  $F$  and  $F'$ , are placed in the positions shown to prevent the concentration changes round the electrodes from affecting the boundaries. Projections at the base of the cups lift them from the electrode vessels and permit the passage of the current.

In order to obtain correct results with the moving-boundary method, the distance through which the boundary moves must be corrected for mass displacement, due to electrochemical reactions which take place at the electrodes during the passage of the current. It was first shown by Miller<sup>2</sup> that if this correction is made the results should be the same as those obtained with the Hittorf method, and shortly afterwards this correction was calculated by Lewis.<sup>3</sup>

In addition to this volume correction, MacInnes and Longworth<sup>4</sup> have pointed out that a second correction must be made for conducting impurities in the solvent.

In Table XXXII are given the results of very accurate transference measurements by the moving-boundary method for a number of electrolytes<sup>5</sup> at 25° C. In this table the results for potassium chloride<sup>6</sup> and lithium chloride<sup>7</sup> are compared with those of Hittorf determinations. The very close agreement between the values obtained by the Hittorf and moving-boundary methods indicates that they measure the same

<sup>1</sup> MacInnes, Cowperthwaite, and Blanchard, *J. Am. Chem. Soc.*, **48**, 1909 (1926).

<sup>2</sup> *Z. physik. Chem.*, **69**, 437 (1909).

<sup>3</sup> *J. Am. Chem. Soc.*, **32**, 862 (1910).

<sup>4</sup> *Chem. Revs.*, **11**, 208 (1932).

<sup>5</sup> Longworth, *J. Am. Chem. Soc.*, **54**, 2741 (1932); **57**, 1185 (1935); MacInnes and Longworth, *Chem. Revs.*, **11**, 210 (1932); *J. Am. Chem. Soc.*, **60**, 3070 (1938).

<sup>6</sup> MacInnes and Dole, *J. Am. Chem. Soc.*, **53**, 1357 (1931).

<sup>7</sup> Jones and Bradshaw, *ibid.*, **54**, 138 (1932).

property of the solution. In spite of its apparent simplicity the values obtained by the Hittorf method are probably the less accurate.

TABLE XXXII  
TRANSFERENCE NUMBERS OF CATIONS AT 25° C

Electrolyte	Method	Concentration			
		0.01 <i>N</i>	0.02 <i>N</i>	0.05 <i>N</i>	0.1 <i>N</i>
AgNO <sub>3</sub>	M.B.	0.4648	0.4652	0.4664	0.4682
HCl	M.B.	0.825 <sub>1</sub>	0.826 <sub>8</sub>	0.829 <sub>2</sub>	0.831 <sub>4</sub>
NaCl	M.B.	0.3918	0.3902	0.3876	0.3854
NaC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	M.B.	.....	0.5549	.....	0.5595
NH <sub>4</sub> Cl	M.B.	0.4908	0.4908	0.4905	0.4907
Na <sub>2</sub> SO <sub>4</sub>	M.B.	0.4625	0.4576	0.4482	0.4375
CaCl <sub>2</sub>	M.B.	.....	0.4220	0.4138	0.4059
LaCl <sub>3</sub>	M.B.	0.4625	0.4576	0.4482	0.4375
KCl	M.B.	0.4903	0.4901	0.4899	0.4898
	Hittorf	.....	0.4893	0.4893	0.4898
LiCl	M.B.	0.3289	0.3261	0.3211	0.3168
	Hittorf	0.329	0.327	0.323	0.319

By means of the moving-boundary method the values 0.442, 0.442, and 0.433 have been obtained for the transference number of the cation of the chlorides of neodymium, samarium, and gadolinium, respectively, in 0.1 normal solution at 25° C;<sup>1</sup> and those of several electrolytes have been measured at 40° C.<sup>2</sup>

TABLE XXXIII  
EXPERIMENTAL TEST OF THE RELATION  $n_c + n_a = 1$

Electrolyte	Concentration	$n_c$	$n_a$	$n_c + n_a$
KCl	0.5	0.488	0.511	0.999
	0.2	0.490	0.510	1.000
	0.1	0.4898	0.5101	0.9999
	0.01	0.4901	0.5097	0.9998
NaCl	0.2	0.3900	0.6099	0.9999
LiCl	0.06402	0.3201	0.6805	1.0006
KBr	0.1	0.4833	0.5165	0.9998
CaCl <sub>2</sub>	0.01904	0.4226	0.5776	1.0002

<sup>1</sup> Haas and Rodebush, *ibid.*, **55**, 3238 (1933).

<sup>2</sup> Samis, *Trans. Faraday Soc.*, **33**, 469 (1937).

By observing the movement of the cation and anion boundaries independent values may be obtained for the transference number of each ion of the electrolyte. The accuracy of the moving-boundary method is indicated by the slight deviation of the sum of these independent values from unity, as illustrated by the data in Table XXXIII.<sup>1</sup>

**Transference Numbers in Solvents Other than Water.** Since equation 12, Chapter V, may be written in the form

$$(u + v)\eta_0 = \text{constant} \quad (9)$$

it follows that the transference numbers of the ions of an electrolyte are independent of the nature of the solvent, for conditions under which the equation holds. However, these numbers might be expected to vary if the degree of solvation of the ions differed in different solvents, or if the molecules of the solvent were associated. An example of variation arising from this cause is found in the transference numbers of the silver ion in 0.01 normal silver nitrate in alcohol-water mixtures:<sup>2</sup>

Wt. % alc.	0	10	30	50	70	90	99.8
$n_c$	0.482	0.482	0.488	0.459	0.446	0.421	0.410

Although the relative mobilities of many ions are the same in water and ethyl alcohol, the hydrogen ion is exceptional. Transference data for alcoholic solutions of hydrogen chloride give  $0.69/0.31 = 2.2$  for the ratio of the mobilities of the hydrogen and chlorine ions, whereas in aqueous solution the ratio is 5.2. It was suggested<sup>3</sup> this behavior indicates that, whereas the ions in salts have approximately the same affinity for water and alcohol, the hydrogen ion has a considerably greater affinity for alcohol.

**Transference in Fused Salts.** A number of investigations have been made of transference phenomena in fused salts and liquid amalgams.<sup>4</sup> In a study of fused  $\text{AlCl}_3\text{-NaCl}$  mixtures, it has been found<sup>5</sup> that for the range 53–57 mole per cent  $\text{AlCl}_3$  the current is carried by the sodium ions, both the aluminum and chlorine being in a complex of small mobility. In their study of transference in the system  $\text{KCl-PbCl}_2$ , Baimakov and Samusenko<sup>6</sup> have found that the best apparatus has three com-

<sup>1</sup> MacInnes and Longworth, *Chem. Revs.*, **11**, 212 (1932).

<sup>2</sup> Krumreich, *Z. Elektrochem.*, **22**, 446 (1916).

<sup>3</sup> Lapworth, *J. Chem. Soc.*, **107**, 857 (1915).

<sup>4</sup> Cf. Schwarz, *Z. Elektrochem.*, **39**, 550 (1933); **45**, 740 (1939); **47**, 144 (1941). For a review of the literature on the subject, see Baimakov and Samusenko, *Trans. Leningrad Ind. Inst.*, **1938**, 3.

<sup>5</sup> Baimakov and Shelomov, *Trans. Leningrad Ind. Inst.*, **1938**, 36 (in English 49).

<sup>6</sup> *Loc. cit.*

partments connected with tubes not less than 3 millimeters in diameter; an insoluble anode is not recommended.

**Hydration of Ions and "True" Transference Numbers.** In the calculation of transference numbers, it has been assumed that only ions migrate through the solution, and that all the water remains stationary during electrolysis. This assumption is not strictly true. Owing to hydration of the ions, water must be carried with them as they move through the solution. Although the amount of water transported in this way is negligible in very dilute solutions, in concentrated solutions it is sufficient to influence the value of the transference numbers. Consequently, values obtained by the Hittorf method do not represent the "true" transference numbers.

Since the ions are hydrated in aqueous solution, it follows that, on the passing of an electric current through a solution of an electrolyte, a transfer of water must take place in the direction of the anode or cathode, according as the degree of hydration of the anion or the cation is greater. If  $n_w$  moles of water are carried from the anode section for each faraday of electricity passed through the solution, then the change in the concentration of the cation in this section is due not only to the migration of  $n_c$  equivalent of the cation, but also to the loss of  $n_w$  moles of water. Thus the decrease in the concentration of the cation in the anode section is less than it would have been, had no water been transferred, by an amount  $n_w(N_s/N_w)$ , where  $N_s$  is the number of moles of solute associated with  $N_w$  moles of water in the original solution. Obviously, this quantity must be added to the Hittorf transference number,  $n_c^H$ , in order to obtain the true transference number,  $n_c^T$ , of the cation. When this correction is made we obtain the relation

$$n_c^T = n_c^H + n_w \left( \frac{N_s}{N_w} \right) \quad (10)$$

Similarly, for the anion,

$$n_a^T = n_a^H - n_w \left( \frac{N_s}{N_w} \right) \quad (10a)$$

In dilute solutions the ratio  $(N_s/N_w)$  is very small and the true transference number is practically identical with the Hittorf transference number. Equations 10 and 10a are important because they afford a means of calculating either the water transference ( $n_w$ ) or the true transference number, provided that the other is known.<sup>1</sup>

<sup>1</sup> The electrolytic transference of water has been studied by M. Taylor and co-workers, *J. Chem. Soc.*, **1929**, 2095; **1932**, 2497; **1937**, 902; Hepburn, *Phil. Mag.*, [vii], **25**, 1074 (1938); Baborovsky, *Trans. Electrochem. Soc.*, **77**, 283 (1939). An experimental method for the direct determination of the ionic transport of water has been developed by Remy, *Z. physik. Chem.*, **89**, 529 (1915).



It was shown by Nernst<sup>1</sup> that the true transference number may be determined experimentally, by adding to the electrolyte certain substances ("reference substances"), such as cane sugar or raffinose, which remain stationary during electrolysis. In this method the ion content at each electrode is determined with respect to the reference substance rather than to water. The change in the amount of water in the vicinity of the electrode is ascertained by measuring the concentration of the reference substance before and after the passage of the current, e.g., by measuring the optical rotation of the solution. The results of measurements with hydrochloric acid<sup>2</sup> and with the alkali chlorides<sup>3</sup> demonstrated the practicability of this method, and Washburn and Millard<sup>4</sup> employed it to determine the true transference numbers given in Table XXXIV.

TABLE XXXIV

"TRUE" TRANSFERENCE NUMBERS AT 25° IN 1.2 NORMAL SOLUTION

Electrolyte	$n_w/n_c^T$	$n_w$	$n_c^T$	$n_c^T$ at Zero Concentration	$n_c^H$
HCl	0.28	0.24	0.844	0.821	0.82
CsCl	0.67	0.33	0.491	0.491	0.485
KCl	1.3	0.60	0.495	0.495	0.482
NaCl	2.0	0.76	0.383	0.396	0.366
LiCl	4.7	1.5	0.304	0.330	0.278

**The Determination of the Composition of Ions by Transference Measurements.** Transference measurements often furnish useful information regarding the nature of the ions in solution. For instance, they may show the presence of complex ions or hydrated ions. When a solution of potassium cuprocyanide is electrolyzed, it is found that the concentration of copper *increases* round the *anode*, showing that copper is contained in a complex negative ion. By means of transference measurements with ammoniacal solutions of copper sulphate and silver chloride, it was shown<sup>5</sup> that the migration of each copper ion to the cathode is associated with the transport of four molecules of  $\text{NH}_3$  in the same direction, and that the complex cation  $\text{Ag}(\text{NH}_3)_2^+$  is transported as such. By the same method, W. A. Noyes and Hibben<sup>6</sup> showed that in

<sup>1</sup> *Göttinger Nachrichten*, **56**, 86 (1900).

<sup>2</sup> Büchbock, *Z. physik. Chem.*, **55**, 563 (1906).

<sup>3</sup> Washburn, *Technology Quarterly*, **21**, 288 (1908); *J. Am. Chem. Soc.*, **31**, 322 (1909); *Z. physik. Chem.*, **66**, 513 (1909).

<sup>4</sup> *J. Am. Chem. Soc.*, **37**, 694 (1915).

<sup>5</sup> Reychler, *Bull. soc. chim. belg.*, **28**, 215, 227 (1914).

<sup>6</sup> *J. Am. Chem. Soc.*, **45**, 355 (1923).

solutions of trimethylhydroxyammonium salts, trimethylmethoxyammonium iodide, trimethylethoxyammonium iodide, and similar salts, an hydroxyl, methoxy, or ethoxy group always remains with the nitrogen as part of the cation. The existence of a  $\text{CuO}_2^{--}$  ion was demonstrated by Creighton,<sup>1</sup> with the aid of transference measurements. Measurements of this kind may also be employed to determine the extent of hydration of ions, as the following considerations<sup>2</sup> indicate.

Evidently, the number of moles of water carried from the anode section for each faraday of electricity passed through a solution is given by the expression

$$n_w = n_c^T N_c - n_a^T N_a \quad (11)$$

where  $N_c$  and  $N_a$  are the average number of moles of water combined with one equivalent of cation and anion, respectively. This expression may be written in the form

$$N_c = \frac{n_w}{n_c^T} + \frac{n_a^T}{n_c^T} N_a \quad (12)$$

by which the relative hydration (or solvation) of ions may be calculated from transference data. On substituting in equation 12 the data given in Table XXXIV, we obtain

$$N_{\text{H}^+} = 0.28 + 0.185N_{\text{Cl}^-} \quad (13)$$

$$N_{\text{Cs}^+} = 0.67 + 1.03N_{\text{Cl}^-} \quad (14)$$

$$N_{\text{K}^+} = 1.3 + 1.02N_{\text{Cl}^-} \quad (15)$$

$$N_{\text{Na}^+} = 2.0 + 1.61N_{\text{Cl}^-} \quad (16)$$

$$N_{\text{Li}^+} = 4.7 + 2.29N_{\text{Cl}^-} \quad (17)$$

From equations 14 and 15, it follows that

$$N_{\text{K}^+} - N_{\text{Cs}^+} = 0.63$$

or that the  $\text{Cs}^+$  ion carries 0.63 mole less water than the  $\text{K}^+$  ion and is, therefore, the least hydrated of the alkali ions. If we assume that (1) zero and (2) four moles of water are combined with the  $\text{Cl}^-$  ion, the corresponding number of moles of water combined with the cations are:

$N_{\text{Cl}^-}$	$N_{\text{H}^+}$	$N_{\text{Cs}^+}$	$N_{\text{K}^+}$	$N_{\text{Na}^+}$	$N_{\text{Li}^+}$
0	0.3	0.7	1.3	2.0	4.7
4	1.0	4.7	5.4	8.4	14.0

<sup>1</sup> *J. Am. Chem. Soc.*, **45**, 1237 (1923).

<sup>2</sup> Washburn and Millard, *J. Am. Chem. Soc.*, **37**, 694 (1915).

All the data given in this and the preceding section are based on the assumption that the reference substances remain absolutely stationary during the passage of the electric current.

**The Absolute Velocities of Ions.** The absolute velocities of the ions of an electrolyte, at zero concentration and under a potential gradient of 1 volt per centimeter, are readily calculated, provided that their transference numbers and the equivalent conductance at zero concentration of the electrolyte are known. On multiplying equation 2 by equation 11, Chapter V, we find that

$$uF = n_c \Delta_0$$

and, therefore, that

$$u = \frac{n_c \Delta_0}{F} \quad (18)$$

Similarly, the velocity of an anion is given by the expression

$$v = \frac{n_a \Delta_0}{F} \quad (18a)$$

Expressed in words: the velocity of an ion is equal to the product of the equivalent conductance at zero concentration of one of its compounds and its transference number in that compound, divided by the faraday. Thus, since the equivalent conductance of silver nitrate at zero concentration is 115.8 at 18° and the transference number of the silver ion in this compound is 0.466 at zero concentration, the absolute velocity of the silver ion at 18° is

$$u = \frac{115.8 \times 0.466}{96,500} \\ = 0.000559 \text{ cm per second}$$

Similarly, the velocity of the nitrate ion is

$$v = 0.000638 \text{ cm per second}$$

Values of the absolute velocities of a number of cations and anions at 18° are given in Table XXXV. The majority of the values in Tables XXXV and XXXVII have been calculated from transference numbers compiled by A. A. Noyes and Falk,<sup>1</sup> and values "adjusted" by Bates<sup>2</sup> for equivalent conductances at zero concentration. The values marked with an asterisk are those given by Kohlrausch:<sup>3</sup>

<sup>1</sup> *J. Am. Chem. Soc.*, **33**, 1456 (1911).

<sup>2</sup> *Berlin Akad. Ber.*, **26**, 586 (1902).

<sup>3</sup> *Ibid.*, **35**, 532 (1913).

TABLE XXXV

SOLUTE VELOCITIES OF IONS AT 18° UND  
OF 1 VOLT PER CENTI

Cation	Velocity cm per sec	Anion	Velocity cm per sec
H <sup>+</sup>	0.003242	OH <sup>-</sup>	0.001802
Cs <sup>+</sup>	0.000698	$\frac{1}{2}$ SO <sub>4</sub> <sup>==</sup>	0.000704
* Rb <sup>+</sup>	0.000684	Br <sup>-</sup>	0.000697
Tl <sup>+</sup>	0.000678	I <sup>-</sup>	0.000685
NH <sub>4</sub> <sup>+</sup>	0.000668	Cl <sup>-</sup>	0.000676
K <sup>+</sup>	0.000665	ClO <sub>4</sub> <sup>-</sup>	0.000670
$\frac{1}{2}$ Ba <sup>++</sup>	0.000569	NO <sub>3</sub> <sup>-</sup>	0.000638
Ag <sup>+</sup>	0.000559	SCN <sup>-</sup>	0.000586
* $\frac{1}{2}$ Sr <sup>++</sup>	0.000559	ClO <sub>3</sub> <sup>-</sup>	0.000569
$\frac{1}{2}$ Ca <sup>++</sup>	0.000534	MnO <sub>4</sub> <sup>-</sup>	0.000553
* $\frac{1}{2}$ Zn <sup>++</sup>	0.000484	IO <sub>4</sub> <sup>-</sup>	0.000494
$\frac{1}{2}$ Cd <sup>++</sup>	0.000476	BrO <sub>3</sub> <sup>-</sup>	0.000494
Na <sup>+</sup>	0.000456	F <sup>-</sup>	0.000483
Li <sup>+</sup>	0.000344	IO <sub>3</sub> <sup>-</sup>	0.000351

The absolute velocities of certain ions have been measured directly. It was shown by Lodge <sup>1</sup> that the mean effective velocity of the hydrogen ion may be determined by allowing these ions to travel through a horizontal tube (Fig. 48) filled with a jelly containing sodium chloride, a drop

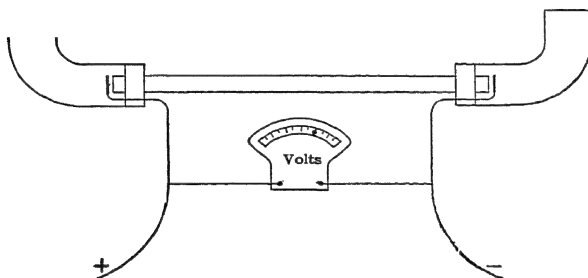


FIG. 48.

or two of sodium hydroxide, and a little phenolphthalein. As the hydrogen ions move forward, their rate of progress is made visible by the decolorization of the jelly. From the potential gradient in the tube, the average velocity of the hydrogen ions under a potential gradient of 1 volt per centimeter may be calculated. The results obtained by Lodge in this way are of the same order of magnitude as those calculated by equation 18; but, owing to the great difficulty of obtaining a uniform

<sup>1</sup> *British Assoc. Advancement Sci. Repts.*, 1886, 389.

potential gradient in the tube, the results cannot be expected to be accurate. The method serves, however, to demonstrate the actual migration of hydrogen ions under the influence of an electric field, and to give an approximate value of the velocity of the hydrogen ion.

Direct measurements of ionic velocities have also been carried out by Whetham.<sup>1</sup> In his experiments he employed two solutions, one of which had a colored ion. The motion of the colored ion was observed, and its velocity calculated under unit potential gradient. In this way, Whetham determined the absolute velocities of the copper, bichromate and chlorine ions. Steele<sup>2</sup> measured the absolute velocities of a number of ions by observing the change in the refractive index of the solution as the ions migrated. The observed and calculated velocities of several of the ions are compared in Table XXXVI.

TABLE XXXVI

VELOCITIES OF IONS UNDER A POTENTIAL GRADIENT  
PER CENTIMETER

Ion	Velocity	Velocity
	cm per-sec (Observed)	cm per sec (Calculated)
H <sup>+</sup>	0.0026	0.0032
Cu <sup>++</sup>	0.00029	0.00031
Cl <sup>-</sup>	0.00058	0.00069
Cr <sub>2</sub> O <sub>7</sub> <sup>--</sup>	0.00047	0.00047

**Ion Conductance.** Instead of the absolute velocities,  $u$  and  $v$ , of the ions, the quantities

$$uF = l_c \quad \text{and} \quad vF = l_a$$

are very frequently employed, so as to avoid small values. These quantities, which are called the **ion conductances**, or the **electrolytic mobilities** of the ions, are 96,500 times larger than the absolute ionic velocities. From equation 11, Chapter V, it follows that

$$\Lambda_0 = l_c + l_a \quad (19)$$

Hence, if the ion conductances are known, the equivalent conductance at zero concentration may be calculated. On combining equation 2 with the preceding equations, we obtain:

$$l_c = \Lambda_0 n_c \quad (20)$$

Similarly,

$$l_a = \Lambda_0 n_a \quad (20a)$$

<sup>1</sup> *Phil. Trans.*, **184**, 337 (1893).

<sup>2</sup> *Ibid.*, **198**, 105 (1902). Cf. Grabe, *Phys. Rev.*, **25**, 249 (1925).

By means of these equations, transference numbers may be calculated from conductance data.

In Table XXXVII are given values of the conductances of a number of cations and anions at 18°, as well as their temperature coefficients,  $\Delta$ .

TABLE XXXVII  
ION CONDUCTANCES AT 18°

Cation	$l_c$	$\Delta$	Anion	$l_a$	$\Delta$
H <sup>+</sup>	313 *	0.0154	OH <sup>-</sup>	174	0.018
Cs <sup>+</sup>	67.4	0.0212	Cl <sup>-</sup>	65.3	0.0216
Rb <sup>+</sup>	66.0	0.0214	Br <sup>-</sup>	67.3	0.0215
K <sup>+</sup>	64.5	0.0217	I <sup>-</sup>	66.1	0.0213
NH <sub>4</sub> <sup>+</sup>	64.5	0.0222	F <sup>-</sup>	46.6	0.0238
Na <sup>+</sup>	43.3	0.0244	ClO <sub>3</sub> <sup>-</sup>	54.9	0.0215
Li <sup>+</sup>	33.1	0.0265	BrO <sub>3</sub> <sup>-</sup>	47.7	.....
Tl <sup>+</sup>	65.5	0.0215	IO <sub>3</sub> <sup>-</sup>	33.9	0.0234
Ag <sup>+</sup>	54.0	0.0229	ClO <sub>4</sub> <sup>-</sup>	64.7	.....
$\frac{1}{2}$ Ba <sup>++</sup>	55.0	0.0239	IO <sub>4</sub> <sup>-</sup>	47.7	.....
$\frac{1}{2}$ Sr <sup>++</sup>	54.0		NO <sub>3</sub> <sup>-</sup>	61.6	0.0205
$\frac{1}{2}$ Ca <sup>++</sup>	51.6	0.0247	C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> <sup>-</sup>	35	0.0238
$\frac{1}{2}$ Mg <sup>++</sup>	45.5	0.0256	HS <sup>-</sup> (0°)	42.5	.....
$\frac{1}{2}$ Pb <sup>++</sup>	61.0	0.0240	MnO <sub>4</sub> <sup>-</sup>	53.4	.....
$\frac{1}{2}$ Cu <sup>++</sup>	45.5		SCN <sup>-</sup>	56.6	0.0221
$\frac{1}{2}$ Zn <sup>++</sup>	46.7		HCO <sub>2</sub> <sup>-</sup>	46.7	.....
$\frac{1}{2}$ Cd <sup>++</sup>	45.9		C <sub>2</sub> H <sub>5</sub> CO <sub>2</sub> <sup>-</sup>	31.0	.....
$\frac{1}{2}$ Fe <sup>++</sup>	45.3		$\frac{1}{2}$ SO <sub>4</sub> <sup>==</sup>	67.9	0.0227
			$\frac{1}{2}$ S <sup>==</sup> (0°)	115	.....

\* Kraus and Parker have obtained the value 315.62, *J. Am. Chem. Soc.*, **44**, 2429 (1922).

The conductances of a number of complex inorganic cations were measured at 25° by Lorenz and Posen.<sup>1</sup> Their results are given in Table XXXVIII.

TABLE XXXVIII  
CONDUCTANCES OF COMPLEX CATIONS AT 25°

Ion	Number of Atoms	Conductance
Co(NH <sub>3</sub> ) <sub>6</sub> <sup>+++</sup>	25	31.4
Co(NH <sub>3</sub> ) <sub>5</sub> Cl <sup>++</sup>	22	34.0
Co(NH <sub>3</sub> ) <sub>5</sub> Br <sup>++</sup>	22	31.6
Co(NH <sub>3</sub> ) <sub>5</sub> NO <sub>3</sub> <sup>++</sup>	25	31.7
Co(NH <sub>3</sub> ) <sub>4</sub> (NO <sub>2</sub> ) <sub>2</sub> <sup>+</sup> ( <i>trans</i> )	23	34.6
Co(NH <sub>3</sub> ) <sub>4</sub> (NO <sub>2</sub> ) <sub>2</sub> <sup>+</sup> ( <i>cis</i> )	23	34.1
Pt(NH <sub>3</sub> ) <sub>4</sub> <sup>++</sup>	17	37.8
Pt(C <sub>6</sub> H <sub>5</sub> N) <sub>4</sub> <sup>++</sup>	45	21.0

<sup>1</sup> *Z. anorg. Chem.*, **96**, 81, 217 (1916).

Except where the hydrogen ion is concerned, the relative values of the conductances of many ions do not appear to be greatly influenced by a change of solvent.

The influence of temperature on ion conductances was very thoroughly studied by Kohlrausch,<sup>1</sup> from whose results were calculated the temperature coefficients given in Table XXXVII. It will be observed that the temperature coefficients are largest for the slowest ions, and *vice versa*. By substituting these values in the equation

$$l_t = l_{18}[1 + (t - 18)\Delta] \quad (21)$$

ion conductances at other temperatures may be calculated. The influence of temperature on the conductances of a number of ions is shown in Table XXXIX.<sup>2</sup>

TABLE XXXIX

ION CONDUCTANCES AT DIFFERENT TEMPERATURES

Temperature	0°	25°	100°
Li <sup>+</sup>	19.3	38.68	121.5
Na <sup>+</sup>	26.1	50.10	152.0
K <sup>+</sup>	40.6	73.50	198.0
Cs <sup>+</sup>	44.4	.....	203.0
Cl <sup>-</sup>	41.2	76.32	208.0
NO <sub>3</sub> <sup>-</sup>	40.0	71.42	186.5
ClO <sub>4</sub> <sup>-</sup>	37.1	.....	176.0

As already mentioned, the equivalent conductances of different electrolytes at zero concentration may be calculated from ion conductances. Thus, at 18°, for potassium chloride,

$$\begin{aligned} \Lambda_0 &= l_{K^+} + l_{Cl^-} \\ &= 64.5 + 65.3 = 129.8 \end{aligned}$$

Moreover, by means of these numbers, the conductances of other ions may be ascertained. If we wish to calculate the conductance of, say, the oxalate ion (C<sub>2</sub>O<sub>4</sub><sup>2-</sup>), it is only necessary to know the equivalent conductance at zero concentration of potassium oxalate and the conductance of the potassium ion. According to Bates,<sup>3</sup> at 18°

<sup>1</sup> *Berlin Akad. Ber.*, **27**, 586 (1902); cf. Lindemann, *Z. physik. Chem.*, **110**, 394 (1924).

<sup>2</sup> Walden and Ulich, *Z. physik. Chem.*, **106**, 49 (1923); MacInnes, Shedlovsky, and Longworth, *J. Am. Chem. Soc.*, **54**, 2758 (1932).

<sup>3</sup> *J. Am. Chem. Soc.*, **32**, 532 (1913).

$$\begin{array}{rcl}
 \Lambda_0 & = & l_{K^+} + l_{\frac{1}{2}C_2O_4^{--}} = 125.5 \\
 \text{Subtracting} & & \underline{l_{K^+}} = \underline{64.5} \\
 \text{there remains} & & l_{\frac{1}{2}C_2O_4^{--}} = 61.0
 \end{array}$$

It will be observed that the values of the conductances of the hydrogen and the hydroxyl ions are much larger than those of other ions, the value of the hydrogen being about five times and that of the hydroxyl about three times greater than the values of the majority of the other ions. These high values explain why, among the strong electrolytes, the acids and bases are far better conductors than the neutral salts. Wannier<sup>1</sup> has pointed out that the mobilities of the hydrogen and hydroxyl ions should approximate the mobility of the sodium ion, and has explained the high observed values on the basis of a proton transfer from one water molecule to the next.

From the results of measurements of transference numbers of sodium and lithium chlorides in water-methyl alcohol mixtures, Longworth and MacInnes<sup>2</sup> have found that the product of the ion conductance and the viscosity markedly deviates from Walden's rule (see equation 12, Chapter V). As a result of this behavior it is concluded that the ion-solvent complex increases in size with increasing methyl alcohol concentration.

**Relations between the Conductances and the Chemical Constitution of the Ions.** The numerical values of the ion conductances exhibit many

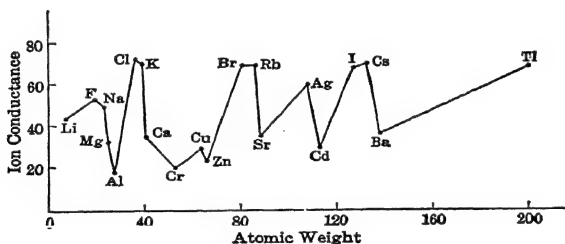


FIG. 49.

regularities. For example, it will be observed (Table XXXVII) that the ion conductances of the alkali metals increase with the atomic weight of the ion, and that this behavior is also true of the alkali-earth ions. On the other hand, the conductances of the oxyhalogen ions decrease as the atomic weight of the ion increases, whereas, with the exception of fluorine, those of the halogen ions are approximately equal. The equal

<sup>1</sup> *Ann. Physik*, [v], **24**, 543 (1935).

<sup>2</sup> *J. Phys. Chem.*, **43**, 239 (1939).



conductances of the halogen ions were attributed <sup>1</sup> to ionic hydration, which counteracted any difference in mobility which might arise from a difference in atomic weight. In a very comprehensive investigation of the conductances of the inorganic ions, Bredig <sup>2</sup> found, in general, that the conductance of an element ion is a periodic function of its atomic weight. This periodic relation is illustrated in Fig. 49.

Much greater regularities were observed with organic than with inorganic ions. The ion conductance of both organic cations and anions steadily decreases as the weight of the ion increases. This behavior is illustrated in Table XL,<sup>2</sup> for the cations of a number of substituted ammonium compounds at 25°.

TABLE XL  
CONDUCTANCES OF ORGANIC CATIONS

Cation	Formula	Number of Atoms	$l_c$
Ammonium	$\text{NH}_4^+$	5	70.4
Dimethylammonium	$\text{NH}_2(\text{CH}_3)_2^+$	11	50.1
Diethylammonium	$\text{NH}_2(\text{C}_2\text{H}_5)_2^+$	17	36.1
Dipropylammonium	$\text{NH}_2(\text{C}_3\text{H}_7)_2^+$	23	30.4
Dibutylammonium	$\text{NH}_2(\text{C}_4\text{H}_9)_2^+$	29	26.9
Diamylammonium	$\text{NH}_2(\text{C}_5\text{H}_{11})_2^+$	35	24.2

The change in the conductance of univalent organic anions with increasing weight is illustrated by the data in Table XLI.<sup>2</sup>

TABLE XLI  
CONDUCTANCES OF ORGANIC ANIONS AT 25°

Anion of	Formula	Number of Atoms	$l_a$
Formic acid	$\text{HCO}_2^-$	4	51.2
Acetic acid	$\text{H}_3\text{C}_2\text{O}_2^-$	7	38.3
Propionic acid	$\text{H}_5\text{C}_3\text{O}_2^-$	10	34.3
Butyric acid	$\text{H}_7\text{C}_4\text{O}_2^-$	13	30.8
Valeric acid	$\text{H}_9\text{C}_5\text{O}_2^-$	16	28.8
Caproic acid	$\text{H}_{11}\text{C}_6\text{O}_2^-$	19	27.4

Bredig also showed that the ion conductances of isomers are approximately equal, provided that the isomers are of analogous constitution. This rule does not apply to metameric ions, however, probably on account of the effect of constitutive influences. With regard to metameric

<sup>1</sup> Euler, *Wied. Ann.*, **64**, 273 (1897).

<sup>2</sup> *Z. physik. Chem.*, **13**, 191 (1894).

nitrogen bases, it may be stated that the conductance of the cations of quaternary bases is greater than that of the cations of tertiary amines, which is greater than the conductance of the cations of secondary amines, and that in turn is greater than the conductance of the cations of primary amines.

**Mobility, Solvation and the Dimensions of Ions.** Attempts have been made <sup>1</sup> to apply Stokes' well-known equation <sup>2</sup> to the motion of ions in an electric field. According to this equation, the velocity of an ion should vary inversely as its radius. Although this has been found to be more or less true for a considerable number of large and heavy ions, the relation does not hold for many simple ions, especially those of the alkali metals. It would be expected that of the ions of the alkali metals the lithium ion should migrate the most rapidly and the caesium ion the least rapidly, since the atomic volumes of these elements increase from lithium to caesium; this, however, is the reverse of what is found. This behavior has been ascribed to solvation of the simple ions; the smaller the actual size of the ion, the more intense the electric field at its surface and, consequently, the greater its tendency to combine with solvent molecules. It has been shown by von Hevesy <sup>3</sup> that nearly all univalent organic ions are so large, and the strength of the electric field with which the ions act on the solvent molecules so correspondingly small, that hydration does not occur. This is in agreement with the results obtained by Lorenz.<sup>4</sup>

A method of calculating the relative sizes of the water envelopes surrounding ions has been suggested by Remy.<sup>5</sup> In this method, which depends upon the assumption that the motion of the ions conforms with the requirements of Stokes' equation, the "apparent radius,"  $r'$ , of an ion is calculated in terms of the radius of the hydrogen ion which is not supposed to be hydrated. For a large number of univalent ions, it has been found that  $r' - r$  (where  $r$  is the true radius of the ion calculated from atomic volume data) is approximately equal to the diameter of a water molecule. In other words, if  $r_w$  is the radius of a molecule of water,

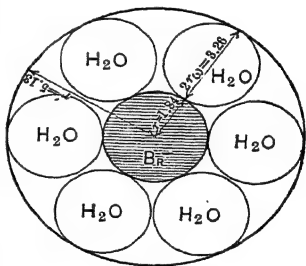


FIG. 50.

<sup>1</sup> Cf. Lorenz and Posen, *Z. anorg. Chem.*, **94**, 265 (1916); Lorenz, *ibid.*, **105**, 175 (1919); *Z. Elektrochem.*, **26**, 424 (1920).

<sup>2</sup>  $u = f/6\pi r\eta$ , where  $u$  is the velocity of a particle of radius  $r$ , moving under a constant force  $f$ , in a medium of viscosity  $\eta$ .

<sup>3</sup> *Z. Elektrochem.*, **27**, 77 (1921).

<sup>4</sup> *Z. anorg. Chem.*, **105**, 175 (1919).

<sup>5</sup> *Z. physik. Chem.*, **89**, 467 (1915). Cf. *ibid.*, **118**, 161 (1925).

then  $(r' - r)/2r_w$  is equal to unity, and these ions are surrounded by a single layer of closely packed water molecules. A diagrammatic representation of an hydrated bromine ion is given in Fig. 50. For bivalent and some univalent ions (e.g.,  $\text{Na}^+$  and  $\text{Li}^+$ ) the value  $(r' - r)/2r_w$  is greater than unity, indicating that the hydration of these ions is greater than that due to a single layer of closely packed water molecules. The number of molecules of water that has been found in this way to be associated with various ions, and the values of  $r$  and  $r'$  expressed in terms of the radius of the hydrogen ion, are given in Table XLII.

TABLE XLII  
HYDRATION AND THE DIMENSIONS OF IONS

$$r_w = 1.626r_{\text{H}^+}$$

Ion	True Radius of Ion	"Apparent Radius" of Ion	$r - r'$	Number of Molecules of Water Associated with an Ion
	$r$	$r'$	$2r_w$	
$\text{Cs}^+$	2.57	5.05	0.8	13
$\text{Rb}^+$	2.21	5.09	0.9	14
$\text{K}^+$	2.20	5.32	1.0	16
$\text{NH}_4^+$	1.99	5.37	1.0	17
$\text{Ti}^+$	1.6	5.21	1.1	16
$\text{I}^-$	1.84	5.17	1.0	15
$\text{Br}^-$	1.84	5.13	1.0	15
$\text{Cl}^-$	1.86	5.25	1.0	16
$\text{NO}_3^-$	2.04	5.57	1.1	19
$\text{OH}^-$	1.47	1.98	0.16	1
$\text{Pb}^{++}$	1.63	5.63	1.2	20
$\text{Ag}^+$	1.33	6.33	1.5	29
$\text{Na}^+$	1.76	7.90	1.9	<66
$\text{Li}^+$	1.42	10.03	2.6	<120
$\text{ClO}_3^-$	2.10	6.12	1.5	26

The question of the hydration of ions has been subjected to rigorous mathematical treatment by Born,<sup>1</sup> who has obtained, for the true and apparent radii of the ions of the alkali metals, values which indicate increasing hydration with decreasing atomic weight, thus explaining the discrepancy mentioned at the beginning of this section.

According to Walden,<sup>2</sup> the magnitude of the ionic radius in non-aqueous solvents follows the same order as in water, viz.,  $\text{H}^+ < \text{K}^+ < \text{Na}^+ < \text{Li}^+$  and  $\text{Br}^- < \text{I}^- < \text{Cl}^- < \text{NO}_3^-$ . The difference between

<sup>1</sup> *Z. Elektrochem.*, **26**, 401 (1920). Cf. Dhar, *Z. anorg. Chem.*, **159**, 57 (1926).

<sup>2</sup> *Z. anorg. Chem.*, **113**, 125 (1920).

the true and apparent radii of these ions is greater in non-aqueous solvents than in water, which is held to indicate a much greater solvation of the ions in the former than in the latter solvent. The degree of solvation decreases with the molecular weight and the complexity of the solvent. Many organic anions and cations have the same radii in water and non-aqueous solvents.

The energy of hydration and the effective radii of ions in solution have been calculated by Webb,<sup>1</sup> starting with the following premises: (1) the energy accompanying the solution of an ion is a free energy change; (2) the dielectric constant of a molecular medium is not constant in the immediate vicinity of an ion;<sup>2</sup> (3) the effective ionic radius is that of a cavity surrounding the ion, in which there are no solvent molecules; and (4) there is an energy change due to compression in the neighborhood of ions. It has been found that the values of the effective radii of a number of ions are about 0.46 angstrom units greater than those obtained by Bragg<sup>3</sup> for crystals. The value obtained for the energy of hydration of the hydrogen ion (several times greater than that for any other ion) and the radius corresponding to this value "seem to indicate that this ion, unlike other common ions, is definitely *chemically* hydrated, probably existing inside one water molecule."

### PROBLEMS

1. Through a 0.1 normal solution of silver nitrate between platinum electrodes 0.001 faraday was passed at 18°. After electrolysis the anode portion yielded 0.0675 gram less silver chloride than the original solution associated with the same weight of water. Calculate the transference number of the nitrate ion in silver nitrate.

2. A solution of potassium chloride containing 0.04024 per cent of chlorine was electrolyzed between a cadmium anode and a platinum cathode, in series with a silver coulometer. After electrolysis it was found that the anode portion, weighing 225.54 grams, contained 0.09971 gram of chlorine; that the middle portion, weighing 185.59 grams, contained 0.07475 gram of chlorine; and that the cathode portion, weighing 327.00 grams, contained 0.12257 gram of chlorine. The silver deposited in the coulometer was the equivalent of 0.01782 gram of chlorine. Calculate the transference numbers of the ions of potassium chloride.

3. A solution of hydrochloric acid was electrolyzed for 45 minutes between a cadmium anode and a platinum cathode, in series with a silver coulometer. At the end of this time it was found that 332.08 grams of the cathode solution contained 0.05759 gram of chlorine, and that the middle solution, which had undergone no change in concentration, contained 0.01790 per cent of chlorine. In the coulometer

<sup>1</sup> *J. Am. Chem. Soc.*, **48**, 2589 (1926); *Proc. Natl. Acad. Sci. U. S.*, **12**, 524 (1926); *Trans. Am. Electrochem. Soc.*, **51**, 559 (1927). For more recent values of ion dimensions, see Van Rysselberghe and Eisenberg, *J. Am. Chem. Soc.*, **62**, 451 (1940).

<sup>2</sup> Cf. Sack, *Physik. Z.*, **27**, 208 (1926).

<sup>3</sup> *Proc. Roy. Inst. Gr. Brit.*, III, **24**, 614 (1925).

0.03320 gram of silver had been deposited. Calculate the transference numbers of the ions of hydrochloric acid.

4. A solution of potassium permanganate was electrolyzed between a platinum cathode and a cadmium anode, in series with a silver coulometer. At the end of electrolysis, 55.05 grams of the cathode solution and 25.00 grams of the middle solution required 64.82 cc and 33.46 cc, respectively, of 0.1 molar oxalic acid solution to cause decolorization. The weight of silver deposited in the coulometer was 0.08481 gram. Calculate the transference numbers of the ions of potassium permanganate.

5. Given that the equivalent conductance at zero concentration of tetramethylammonium chloride is 113.8 at 18°, and that the transference number of the cation is 0.383, calculate the velocities of the ions of this salt.

6. At 25° the equivalent conductance of  $\frac{1}{32}$  normal tetraethylarsonium chloride is 85.5 and its conductance ratio is 0.854. Given that the transference number of the cation in this compound is 0.298, calculate the conductance of each ion.

7. It has been found that at 25° the equivalent conductance at zero concentration of sodium trichloracetate is 82.0, and that the transference number of the anion is 0.40. Given that  $\Lambda_0^{\text{KCl}} = 140.8$  and that  $n_{\text{K}^+} = 0.501$ , calculate the equivalent conductance at zero concentration of potassium trichloracetate at 25°.

8. At 18°, the velocities of the cation and anion of valerianic acid are 0.003242 and 0.0002662 cm per second. Given that the temperature coefficients of the conductances of these ions are 0.0154 and 0.0244, respectively, calculate the equivalent conductance at zero concentration of the acid at 25°.

9. Estimate the specific conductance of a water containing 70 parts per million of calcium sulphate.

10. A 0.01 molal solution of lithium chloride has a specific conductance of 0.000936 mho at 18°. With the aid of data given in Table XXIX, calculate the ion conductances.

## CHAPTER VII

### ELECTROKINETIC PHENOMENA

**Electrical Migration.** In the determination of transference numbers, it is not practicable to separate the anode and cathode sections of the electrolysis cell by means of a porous diaphragm, owing to the fact that during electrolysis of dilute aqueous solutions not only positively charged cations, but also water molecules (in addition to those carried by the hydrated cation), migrate to the cathode section, simultaneously decreasing the amount of solvent in the anode section. The more dilute the electrolyte, the more noticeable is this phenomenon of water migration towards the cathode. It may be observed in the electrolysis of a 0.01 normal solution of sulphuric acid, when the solution is divided into an anode section and a cathode section by means of a porous clay diaphragm, such as a porous battery jar. With a 0.001 or a 0.0001 normal solution of the acid the anode section may be emptied in a few minutes if a sufficiently high electromotive force is employed.

The movement of a *liquid* across a diaphragm or through a capillary tube, under the influence of a potential difference, was first observed by Reuss in 1807. To this phenomenon the name **electro-osmosis** was given. It was found that the occurrence of electro-osmosis depends on the fact that, when a solvent is in contact with any heterogeneous substance, the two phases acquire unlike charges resulting in a potential difference between them. Consequently, if one of the phases is free to move, it will migrate to one or other of the electrodes under the influence of an electric field. In the example just considered, the water becomes charged positively, and the porous clay diaphragm negatively. Hence, since the water is free to move, it migrates to the cathode. As most substances become negatively charged when in contact with water, the water, positively charged, usually migrates to the cathode.

If, however, instead of having a liquid in contact with an immovable solid, solid particles are suspended in a liquid, then, since these particles are free to move and no permanent difference in level can persist in the liquid, the *solid* particles will migrate to one or other of the electrodes. This movement of suspended particles is known as **electrophoresis** or **cataphoresis**. Although the terms "electro-osmosis" and

"electrophoresis" are sometimes used synonymously, it is well to employ them in the sense here indicated, so as to distinguish between the two phenomena. Both phenomena have been investigated extensively.<sup>1</sup>

Both electro-osmosis and electrophoresis have been observed with liquids other than water; for example, with methyl and ethyl alcohols, acetone, nitrobenzene, and pyridine. Quinke found that, whereas, with diaphragms of many different materials, such as silk, clay, and asbestos, water migrated to the cathode, turpentine moved to the anode. Coehn<sup>2</sup> explained this behavior on the assumption that "if two heterogeneous substances are in contact, the one with the higher dielectric constant is positively charged with respect to the other." This statement is known as Coehn's rule. For example, when glass ( $\epsilon = 5-10$ ) is immersed in water ( $\epsilon = 81$ ), it becomes negatively charged; when immersed in turpentine ( $\epsilon = \text{ca. } 2$ ), it becomes positively charged. In accordance with Coehn's rule, the very high dielectric constant of water would account for the fact that water is usually positively charged when in contact with other substances. However, Briggs<sup>3</sup> showed that this rule is by no means absolute, even for pure liquids, and that it fails entirely when applied to solutions. McLaughlin<sup>4</sup> found that air bubbles ( $\epsilon = \text{ca. } 1$ ) when suspended in water migrated to the anode, but when suspended in benzene ( $\epsilon = \text{ca. } 2$ ) and in nitrobenzene ( $\epsilon = 35-38$ ) they traveled to the cathode.

That the analogy between suspended (colloidal) particles and ions is a very close one was shown by the results of calculations based on Stokes' equation.<sup>5</sup> In consequence of their charge suspensoids conduct the electric current, the conductance increasing as the radii of the particles increase. However, even with particles having a radius of  $10^{-7}$  centimeter, the conductance is very small; it would appear to be always less than that of a 0.0001 normal salt solution. This is attributed to the relatively small number of particles present, for their charge is always greater than that of an ion of the same size.

<sup>1</sup> Cf. Wiedermann, *Pogg. Ann.*, **87**, 321 (1856); Quinke, *ibid.*, **107**, 1 (1859); **110**, 38 (1860); **113**, 513 (1861); Helmholtz, *Wied. Ann.*, **7**, 337 (1879); Lamb, *Phil. Mag.*, **26**, 52 (1888); Perrin, *J. chim. phys.*, **2**, 601 (1904); **3**, 50 (1905); Burton, *Phil. Mag.*, **11**, 425 (1906); **12**, 472 (1906); Briggs, *J. Phys. Chem.*, **21**, 198 (1917). The British Association for the Advancement of Science, **1918**, "Report on Colloidal Chemistry," pp. 26-39, contains a bibliography to the end of 1917. For early literature, see Wiedermann, *Elektrizität*, **1**, 993 (1893). For a review and discussion of the conditions of electrokinetic phenomena, see Labes, *Z. physik. Chem.*, **116**, 1-64 (1925).

<sup>2</sup> *Wied. Ann.*, **64**, 217 (1898).

<sup>3</sup> *J. Phys. Chem.*, **21**, 198 (1917).

<sup>4</sup> *Sci. Proc. Roy. Dublin Soc.*, **17**, 13 (1922).

<sup>5</sup> Michaelis, *Kolloid Z.*, **31**, 246 (1922).

**The Origin of the Electric Charge.** Although various theories<sup>1</sup> have been put forward to account for the origin of the electric charges acquired by dissimilar phases in contact, no one of them is wholly satisfactory. Formerly, it was assumed that the source of the charge was essentially physical. According to the Helmholtz-Lamb hypothesis, the two phases become oppositely charged in a manner analogous to the production of electrification in frictional electricity. In this way an electric "double layer" is produced, as illustrated in Fig. 51, where the

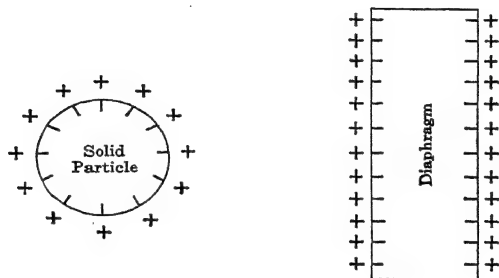


Fig. 51.

molecules of the liquid are represented as being positively charged and the solid phase as carrying a negative charge.<sup>2</sup> It must be assumed that there is a certain slip or "give" ("facility of slip") between the two coatings of the electric double layer; otherwise there could be no motion of the solid or liquid phase in an electric field. In electrophoresis, for example, the first stage "must be, therefore, a polarization of the colloid-medium system [solid-liquid phases], followed by a transfer of the charge on the layer, made up of the molecules of the medium [liquid], to other contiguous molecules. In this way the particle is handed on, so to speak, by the molecules of the medium."<sup>3</sup>

Although there is much evidence in harmony with this view,<sup>4</sup> the results of several investigations support the hypothesis of Freundlich<sup>5</sup> and Bancroft,<sup>6</sup> according to which the origin of the charge is to be

<sup>1</sup> For a critical analysis of these theories, see Briggs, *loc. cit.*

<sup>2</sup> The theory and structure of the electric double layer have been discussed by Gouy, *Ann. phys.*, **7**, 129 (1917).

<sup>3</sup> W. C. McC. Lewis, *A System of Physical Chemistry*, Vol. 1, p. 335, 1929.

<sup>4</sup> See Donnan, *Rept. Brit. Assoc. Advancement Sci.*, **1920**, 1. See also the work of Beans and Eastlack, *J. Am. Chem. Soc.*, **37**, 2667 (1915); Gyemant, *Kolloid Z.*, **28**, 103 (1921); Powis, *J. Chem. Soc.*, **107**, 818 (1912).

<sup>5</sup> *Kapillarchemie*, **1909**, 245.

<sup>6</sup> *Trans. Am. Electrochem. Soc.*, **21**, 233 (1912)



attributed to selective adsorption of the ions by the solid phase. The sign of the charge on this phase depends upon the relative adsorption of the cations and anions, being positive if the former are adsorbed to a greater extent than the latter, and *vice versa*. It follows from this hypothesis that any change in the character of the adsorption will exert an influence on electrokinetic behavior.

A metallic hydroxide when suspended in water becomes positively charged and the water becomes negatively charged. Since water contains a very small, but measurable, concentration of hydrogen and hydroxyl ions, the positive charge on the hydroxide may be explained on the assumption that the suspended particles adsorb some of the hydrogen ions present in the water, thus leaving the water negatively charged by an excess of hydroxyl ions. This assumption is substantiated by the fact that it has been found that a film of aluminum hydroxide is permeable to hydrogen ions, but not to hydroxyl ions. Indeed, as Taylor and Inglis<sup>1</sup> showed, hydroxyl ions cannot be driven through a membrane of aluminum hydroxide, even by a high electromotive force. Regarding the adsorption of ions by solids Briggs<sup>2</sup> stated:

"We may postulate that every solid has a specific adsorbing power for a given ion, which depends upon the specific surface of the solid, upon the temperature, upon the concentration of the particular ion in the solution, and upon the other ions present or adsorbed previously by the solid. When the ion content of the liquid is vanishingly small, we shall have but little ion adsorption and little electro-osmosis. Non-dissociated and non-dissociating liquids show little electro-osmosis, an experimental confirmation of the preceding statement. On the other hand 'pure' water shows marked endosmosis through many solids. This is a case of preferential ion adsorption where the ions are produced both from the ionization of water itself and the solution of the solid which is a very important matter in some cases. Now, since the majority of solids are negative against water, we postulate that hydroxyl ions are adsorbed in preference to hydrogen ions. Freshly precipitated alumina is reported to be electro-positive; my idea regarding this is not that alumina on dissolving sends out rapidly diffusing hydroxyl ions and becomes positive against the solution, but that it adsorbs aluminium or hydrogen ions more easily than hydroxyl ions . . . . In discussing the potential of a solid against water *originally pure*, we must accordingly take two factors into account:

"1. The specific adsorption capacity of the solid for hydrogen and hydroxyl ions produced by the dissociation of water.

<sup>1</sup> *Phil. Mag.*, 5, 301 (1903).

<sup>2</sup> *Loc. cit.*

"2. The solution of the solid, which though extremely small in many cases, may produce ions that are strongly adsorbed."

Although the Freundlich-Bancroft hypothesis satisfactorily explains electrokinetic phenomena in water and solutions and appears to be essentially correct, the selective adsorption of ions does not adequately explain the source of the original charge on a solid phase in contact with pure liquids which cannot be regarded as being capable of giving rise to ions, even in the minutest amount. In view of the results of Langmuir <sup>1</sup> and of Harkins and his associates <sup>2</sup> on the conditions existing at the surface of a liquid, Strickler and Mathews <sup>3</sup> suggest that the charge is due to an orientation of the molecules of the liquid at the surface and within the pores of the solid phase. This orientation depends on the nature of both phases, and, accordingly, a salt dissolved in the liquid would either increase or decrease the charge on the solid phase by selective adsorption.

**Structure and Properties of the Double Layer.** Owing to the difficulty of adequately accounting for electrokinetic phenomena on the basis of a double layer having a structure such as that depicted in the preceding section, various other structures have been proposed from time to time. It was postulated <sup>4</sup> that the double layer, instead of being sharp on the liquid side, diffuses for some distance into the liquid phase. Although the effect of the diffusion tendency is appreciable in the outer part of the double layer, its influence on the rigidity of the inner part is probably small, owing to the very large adsorption forces. Accordingly, Stern <sup>5</sup> considered the double layer to be a condenser, one side of which is the solid surface having attached to it a rigid layer ( $\Delta B$ , Fig. 52) of approximately molecular thickness; and beyond this a diffuse layer extending into the liquid, as indicated in Fig. 52. Part of the electric charge is concentrated in the surface, while the density of that in the liquid diminishes asymptotically to zero.

The fall in potential in the fixed layer is sharp and in the diffuse layer

<sup>1</sup> *J. Am. Chem. Soc.*, **39**, 1848 (1917).

<sup>2</sup> *Ibid.*, **39**, 354 (1917).

<sup>3</sup> *Ibid.*, **44**, 1644 (1922).

<sup>4</sup> Cf. Billiter, *Z. physik. Chem.*, **45**, 307 (1903); Gouy, *J. phys.*, [v], **9**, 457 (1910); Chapman, *Phil. Mag.*, [vi], **25**, 475 (1913).

<sup>5</sup> *Z. Elektrochem.*, **30**, 508 (1924). For discussions of the properties of the double layer see Freundlich and Rona, *Preusz. Akad. Wiss.*, **20**, 397 (1920); von Smoluchowski, Article in Graetz, *Handb. d. Elek. und d. Magnetismus*, Barth, Leipzig, **2**, 366 (1921); Gyemant, *Z. physik. Chem.*, **100**, 182, **102**, 74, **103**, 260 (1922); *ibid.*, **108**, 387 (1924); Mooney, *J. Phys. Chem.*, **35**, 331 (1931); Verwey, *Chem. Revs.*, **16**, 363 (1935); Craxford, *Trans. Faraday Soc.*, **35**, 85 (1940); Krut and Overbeck *ibid.*, **35**, 110 (1940); Bikerman, *ibid.*, **35**, 154 (1940).

gradual. The total potential fall in the two layers is the so-called **epsilon potential** ( $\epsilon$ ), also known as the electrochemical or thermodynamic potential; that in the diffuse layer is designated the **zeta potential** ( $\zeta$ ). In a study of layers of proteins on glass, Abramson found<sup>1</sup> that, whereas the  $\zeta$  potential was determined by the plane of shear and was fixed by the ions at that point, the  $\epsilon$  potential seemed to be independent of the adsorbed layer and was identical for all films. These two potentials not only may differ, but also they may be of opposite sign.

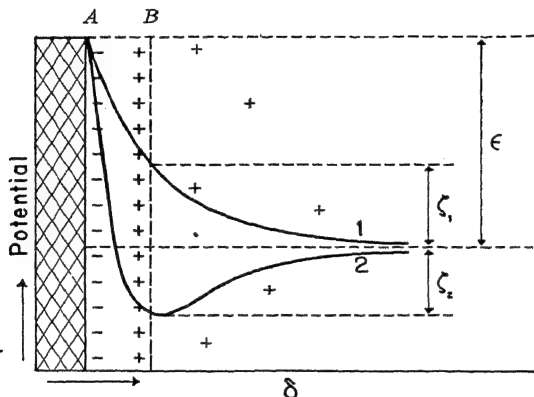


FIG. 52.

This behavior is indicated graphically in Fig. 52,<sup>2</sup> in which the solid phase is to the left of A and the movable liquid phase is to the right of B. The region AB represents the film adhering rigidly to the surface of the solid phase.

The  $\zeta$  potential, which is intimately associated with electrokinetic phenomena, is given by the equation

$$\zeta = \frac{4\pi e\delta}{\epsilon} \quad (1)$$

In this expression  $e$  is the charge on unit surface,  $\delta$  the distance between the two sides of the double layer, and the other quantities have their usual significance. From equation 1 it is evident that both changes in the thickness of the double layer and the charge density, due to variation in the number of ions adsorbed, will alter the value of the  $\zeta$  potential.

<sup>1</sup> Cf. *Electrokinetic Phenomena*, p. 124, New York, 1934.

<sup>2</sup> After von Smoluchowski, *loc. cit.*

Measurements of the  $\epsilon$  and  $\zeta$  potentials on the same sample of glass in dilute solutions of aqueous electrolytes were carried out by Freundlich and Ettisch,<sup>1</sup> whose results are given in Table XLIII. The different methods of measuring the  $\zeta$  potential have been discussed by Moyer.<sup>2</sup>

TABLE XLIII

INFLUENCE OF SALTS ON THE  $\epsilon$  POTENTIAL AND THE  $\zeta$  POTENTIAL

Salt	Molar Concentration			
	$10^{-7}$	$10^{-6}$	$10^{-5}$	$10^{-4}$
$\epsilon$ potential in millivolts				
KCl	- 92	- 84	- 63	- 54
BaCl <sub>2</sub>	-120	-108	-103	-92
La(NO <sub>3</sub> ) <sub>3</sub>	- 89	- 64	- 56	-38
Th(NO <sub>3</sub> ) <sub>4</sub>	-134	-120	- 88	-46
$\zeta$ potential in millivolts				
KCl	- 35	- 38	- 22	- 4
BaCl <sub>2</sub>	- 29	- 26	- 17	- 3
La(NO <sub>3</sub> ) <sub>3</sub>	- 11	- 7	- 1	- 0.5
Th(NO <sub>3</sub> ) <sub>4</sub>	- 3	+ 21	+ 16	+ 4

**Electro-Osmosis.** Electro-osmosis is influenced by many factors. The direction of electro-osmotic flow depends upon the sign of the charge on the diaphragm. The rate of flow is proportional to the intensity of the charge on the diaphragm, provided that the potential gradient through the diaphragm is constant. With the same diaphragm, electro-osmotic flow varies both in direction and rate with the nature of the liquid, as shown in Table XLIV, which gives results obtained by Strickler and Mathews with a filter-paper diaphragm.

For a given liquid Wiedermann found that "the quantity of liquid carried through a porous diaphragm, in a definite time, varies directly as the current strength and is independent of the area and thickness of the diaphragm." He also found that the rate of flow varies directly as

<sup>1</sup> *Z. physik. Chem.*, **116**, 401 (1925).

<sup>2</sup> *Trans. Electrochem. Soc.*, **73**, 481 (1938). Cf., also, Bikerman, *J. Phys. Chem.*, **46**, 724 (1942).

TABLE XLIV

RATE AND DIRECTION OF ELECTRO-OSMOSIS WITH DIFFERENT LIQUIDS

Liquid	Electrode towards Which Liquid Flows	Volume of Flow, cc/sec
Amylene	+	Very slight
Toluene	-	0.0012
Benzene	-	0.0009
Xylene	-	0.0006
Carbon bisulphide	+	0.0007
Ether	+	0.0011
Chloroform	+	0.0038
Isoamylformate	-	0.053
Aniline	+	0.074
Propyl alcohol	+	0.077
Ethyl propionate	+	0.483

the applied electromotive force. The results obtained by Strickler and Mathews show, however, that the rate of flow is not quite a linear function of the voltage (Fig. 53), and that in the apparatus used by them the

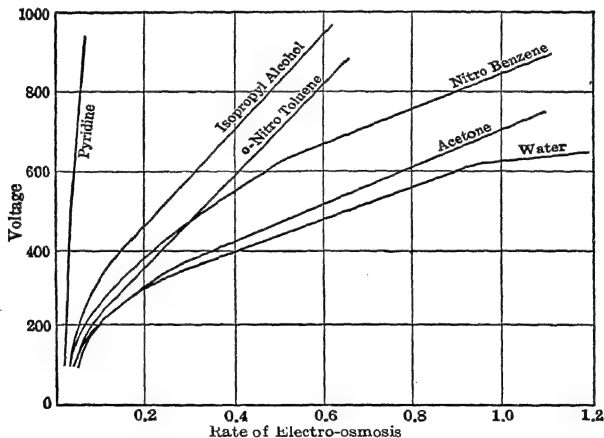


FIG. 53.

permeability of the diaphragm is an important factor. For a given potential difference, the rate of flow increases with rise in temperature, the increase being somewhat smaller than that of the fluidity of the liquid. The influence of temperature on the rate of electro-osmosis

of a number of liquids is shown by Strickler and Mathews' curves in Fig. 54. Among other factors which play a role in electro-osmosis may be mentioned the following:<sup>1</sup> the kind and arrangement of the diaphragm; the kind, concentration, and reciprocal action of electrolytes; the adsorption relation of the diaphragm towards electrolytes; and the presence of colloids or crystalloid non-electrolytes in the liquid.

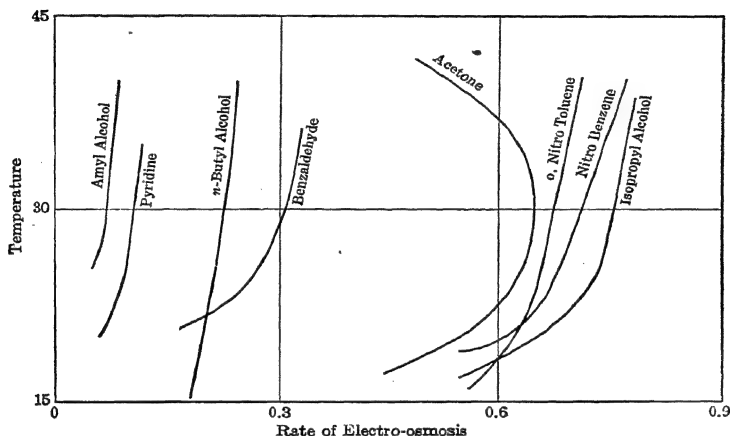


FIG. 54.

The influence of the nature of the diaphragm on electro-osmosis is illustrated by the following data obtained by Remy.<sup>2</sup> Using conductance water, he found that the electro-osmotic flow amounted to 373,000, 23,000, 2350, 886 and 372 cubic centimeters, per faraday, with Zsigmondy's membrane, clay, gelatine, parchment, and animal charcoal diaphragms, respectively. Parchment is, therefore, an ideal diaphragm material to use for differentiating between electro-osmotic and ionic transfer of water, especially as above a certain concentration the former decreases as the concentration of the electrolyte increases. Remy showed that with a parchment diaphragm the transfer of water in 1.0 and 0.1 normal solutions of a large number of electrolytes is practically wholly due to the movement of hydrated ions. Kahlenberg<sup>3</sup> found that india rubber is a good diaphragm material for use with organic solvents.

<sup>1</sup> Prausnitz, *Kolloid Z.*, **29**, 293 (1919).

<sup>2</sup> *Z. Elektrochem.*, **29**, 364 (1923); *Z. physik. Chem.*, **118**, 161 (1925).

<sup>3</sup> *J. Phys. Chem.*, **10**, 141 (1906).

Various types of apparatus have been employed for studying electro-osmosis. An improved form <sup>1</sup> of Perrin's electro-osmometer is shown in Fig. 55. This instrument is designed to eliminate errors produced by evolution of gas at the electrodes. It consists essentially of a horizontal tube containing the diaphragm *D*, in close proximity to which are the electrodes *A* and *C*, contained in vertical side tubes which permit the escape of gases generated by the passage of the current. The anode and cathode compartments are joined (by means of rubber connections *R*) to

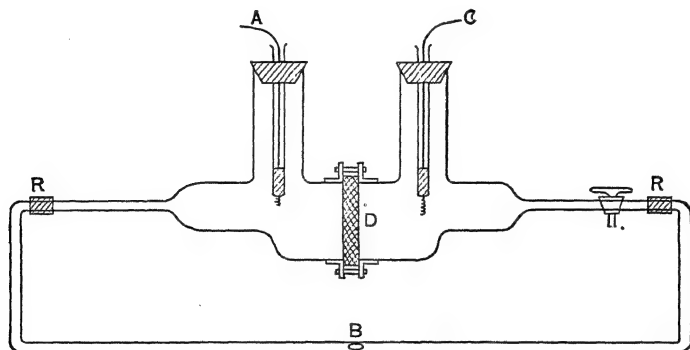


FIG. 55.

a narrow tube which contains an air bubble, *B*. This tube is provided with a scale, and the rate at which the bubble moves gives a measure of the electro-osmotic flow.

**The Influence of Electrolytes on Electro-Osmosis.** In his studies of the influence of the presence of acids, alkalis, and neutral salts on electro-osmosis, Perrin found that these substances produced a change in the potential difference existing between water and a solid phase. His experiments showed that negative diaphragms became more negative on the addition of an alkali, and less negative on the addition of an acid. With increasing concentration of acid, negative diaphragms may become electrically neutral and, finally, positive. Positive diaphragms behave in a reverse, but corresponding manner. Perrin's data, in Table XLV, show the influence of additions of hydrochloric acid and potassium hydroxide on the potential difference existing between water and two diaphragms, Carborundum and naphthalene. The + or - sign denotes the charge on the diaphragm, and also the electrode to which a volume,

<sup>1</sup> Cf. Briggs, Bennett, and Pierson, *J. Phys. Chem.*, **22**, 256 (1918); Strickler and Mathews, *loc. cit.* Cf. Fairbrother and Mastin, *J. Chem. Soc.*, **125**, 2319 (1924).

$v$ , of water migrates in unit time. The reversal of the direction of electro-osmotic flow observed by Perrin was confirmed by Briggs, Bennett, and Pierson,<sup>1</sup> who, with a Carborundum diaphragm, found that the isoelectric point <sup>2</sup> (i.e., the point at which the potential difference between the liquid and the diaphragm is zero) corresponded to a very slightly acid solution. Sharp reversals were also obtained with diaphragms of

TABLE XLV

INFLUENCE OF ACIDS AND ALKALIS ON ELECTRO-OSMOTIC FLOW

Normal Concentration of Acid or Alkali	$v$ cc/min	
	Carborundum Diaphragm	Naphthalene Diaphragm
0.02 HCl	+ 10	+38
0.008 HCl	± 0	....
0.002 HCl	- 15	....
0.001 HCl	....	+28
0.0002 HCl	....	+ 3
Distilled water	- 50	....
0.0002 KOH	- 60	-29
0.002 KOH	-105	-60
0.02 KOH	....	-60

other substances. The influence of different concentrations of acid and alkali on the rate and direction of electro-osmosis of water with a naphthalene diaphragm (Perrin) and of amyl alcohol with a filter paper diaphragm (Strickler and Mathews) is shown graphically in Fig. 56.

The influence of salt additions is similar to that of acids and bases. From the results of his investigations, Perrin enunciated the following generalization, which is sometimes called Perrin's valence rule: *the greater the valence of the cation of the added salt, the greater the decrease in the potential difference between a negative diaphragm and the solvent; and the greater the valence of the anion of the added salt, the greater the decrease in the potential difference between a positive diaphragm and the solvent.* In the first case the valence of the anion, and in the second the valence of

<sup>1</sup> *J. Phys. Chem.*, **22**, 256 (1918). Cf. Fairbrother and Mastin, *J. Chem. Soc.*, **127**, 322 (1925).

<sup>2</sup> The general theory of the isoelectric point has been discussed by Bikerman, *J. Phys. Chem.*, **46**, 724 (1942).



the cation, has little or no influence on the potential difference between the diaphragm and the solvent. The influence of ionic valence on electro-osmosis was also studied by Freundlich, whose results were in accordance with the valence rule.<sup>1</sup>

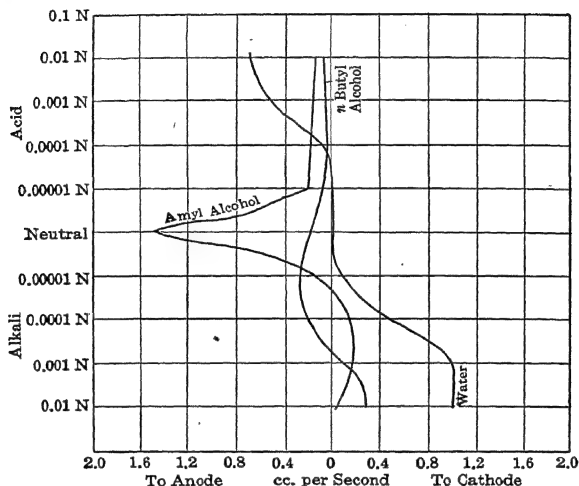


FIG. 56.

The valence rule, though a useful guide, was found to hold only to a limited extent.<sup>2</sup> Bancroft<sup>3</sup> showed, however, that certain exceptions to the rule were only apparent and not real:

"If we take an acidified copper sulphate solution and a porous clay cup we find that electrical endosmose carries the solution through the walls of the cup from the anode to the cathode which is not the direction Perrin's law would lead us to expect. On the other hand the solution passes to the anode if we substitute copper nitrate and nitric acid for the corresponding sulphates. The sign of the charge on a diaphragm depends on the relative adsorption of cation and anion . . . . Let us assume that for equal concentrations hydrogen as ion is adsorbed somewhat more readily than sulphate as ion, while copper as ion and nitrate as ion are only adsorbed to a relatively slight extent. In that case the diaphragm will be charged positively in sulphuric acid and nitric acid; but will be charged negatively in copper sulphate. Electrical endosmose will

<sup>1</sup> *Kapillarchemie*, 1909, 238.

<sup>2</sup> Cf. Elissaffoff, *Z. physik. Chem.*, **79**, 385 (1912).

<sup>3</sup> *Trans. Am. Electrochem. Soc.*, **21**, 233 (1912).

then carry sulphuric acid and nitric acid solutions to the cathode and a copper sulphate solution to the anode, which is what happens. An acidified copper nitrate solution will also move to the anode because hydrogen as ion will be the deciding factor. The situation is different in an acidified copper sulphate solution, especially if the concentration of copper sulphate is high and that of sulphuric acid is low. Since the adsorption of sulphate as ion increases with increasing concentration, there will come a point at which sulphate as ion is adsorbed more strongly than hydrogen as ion. The charge on the diaphragm will then reverse and electrical endosmose will carry the solution through the diaphragm from the anode to the cathode, which is what happens experimentally."

**The Rate of Electro-Osmotic Flow.** In order to calculate the rate of flow, let us consider a liquid moving with a velocity  $u$ , through a capillary tube of cross section  $q$ , under the influence of an electric field produced by an electromotive force  $E$  applied to electrodes. As we have seen, an electric double layer is formed at the surfaces of contact of the liquid and the tube. If it is assumed that the solid portion of the double layer does not exist in the solid itself, but in a film of liquid adhering immovably to the solid, then the frictional force  $f$  resisting the moving liquid is directly proportional to the coefficient of viscosity  $\eta$ , the velocity of the liquid, and the area of the moving surface of the electric double layer, and inversely proportional to the distance  $\delta$  between the two sides of the electric double layer. For unit surface

$$f = \frac{\eta u}{\delta}$$

But since

$$u = \frac{v}{q} \quad (2)$$

where  $v$  is the volume of liquid which passes through a cross section of the tube in unit time,

$$f = \frac{\eta v}{\delta q}$$

If we represent the charge on unit surface of the moving side of the electric double layer by  $e$ , and the potential gradient in the tube by  $X$ , then the electric force acting on unit surface of the moving layer is  $eX$ . Since this is the force necessary just to overcome the frictional force, and to impart a constant velocity to the moving side of the electric double layer, we may write

$$eX = \frac{\eta v}{\delta q} \quad (3)$$

If we regard the electric double layer as a condenser of potential  $\zeta$ , in a medium having a dielectric constant  $\epsilon$ , its capacity per unit area is

$$\frac{c}{\zeta} = \frac{\epsilon}{4\pi\delta}$$

whence

$$\zeta = \frac{4\pi\delta e}{\epsilon}$$

On combining this with equation 3, we obtain

$$\zeta = \frac{4\pi\eta v}{\epsilon q X}$$

or

$$v = \frac{q \cdot \epsilon \cdot \zeta \cdot X}{4\pi\eta} \quad (4)$$

Since the potential gradient,  $X$ , is equal to the electromotive force applied to the electrodes divided by the distance,  $l$ , between them, we may write:

$$v = \frac{q \cdot \epsilon \cdot \zeta \cdot E}{4\pi \cdot \eta \cdot l} \quad (5)$$

Expressed in words: the volume of liquid transported by electro-osmosis through a cross section of a tube, in unit time, is directly proportional to the area of the cross section, the dielectric constant of the liquid, the potential of the electric double layer, and the external electromotive force, and inversely proportional to the viscosity of the liquid and the distance between the electrodes.

From equation 1, Chapter I, and the relation

$$R = \frac{l}{\kappa q}$$

where  $\kappa$  is the specific conductance of the liquid, it follows that

$$E = \frac{Il}{\kappa q}$$

On substituting this value of  $E$  in equation 5, we get

$$v = \frac{\epsilon \cdot \zeta \cdot I}{4\pi\eta\kappa} \quad (6)$$

That is: for a given current strength, the quantity of liquid transported through a cross section of a tube, in unit time, is independent of the area of the cross section and the distance between the electrodes.

In employing the preceding equations, as well as those which follow in this chapter, all quantities must be expressed in absolute units. To express volts and amperes in absolute (electrostatic) units, volts must be multiplied by  $1/300$  and amperes by  $3 \cdot 10^9$ .

**The Pressure Equation.** If electro-osmosis takes place in such a way that a difference in level results in a capillary tube, or in a tube containing a diaphragm, an hydrostatic pressure will be established. This pressure ultimately attains a maximum value, when it becomes equal to the force which causes the liquid to move in the tube. The volume of liquid which flows through a capillary tube in unit time is given by Poiseuille's law

$$v = \frac{\pi P r^4}{8 \eta l} = \frac{P q r^2}{8 \eta l}$$

where  $P$  is the pressure, and  $l$  and  $r$  the length and radius, respectively, of the tube. It follows from equation 5 that

$$\frac{P \cdot q \cdot r^2}{8 \cdot \eta \cdot l} = \frac{q \cdot \epsilon \cdot \zeta \cdot E}{4 \pi \eta l}$$

and, therefore, that

$$P = \frac{2 \cdot \epsilon \cdot \zeta \cdot E}{q} \quad (7)$$

Accordingly, for a capillary tube of given material, the maximum hydrostatic pressure produced by electro-osmosis is directly proportional to the potential difference between the electrodes and the dielectric constant of the liquid, and inversely proportional to the cross section of the tube.

**Electrophoresis.** As already pointed out, this phenomenon is the reverse of electro-osmosis: instead of the liquid, the solid phase is free to move, and it migrates to the anode or the cathode according to whether it is negatively or positively charged, or perhaps both phases move in opposite directions. Here we are dealing with a mobile diaphragm. When suspended in water, particles of the following substances are negatively charged with respect to the liquid and, therefore, migrate to the anode: sulphur, clay, shellac, starch, most metals and many metallic compounds in the colloidal state, and a large number of organic sols. The hydroxides of the metals, titanin acid, methyl violet, methylene blue, magdala red, etc., are positively charged and move to

the cathode. Most of the conclusions relating to electro-osmosis also hold for electrophoresis.

The influence of electrolytes on electrophoresis has been extensively studied. It has been found<sup>1</sup> that the charge on particles of mastic, gamboge, and arsenic trioxide (negative colloids) in water decreases with increasing concentration of hydrogen ions, but that a reversal of the sign of the charge does not occur; ferric hydroxide (positive), on the other hand, behaves in the same way with hydroxyl ions.

It has long been known that, when very small quantities of certain electrolytes are added to suspensoids, electrophoresis stops, and that coagulation and precipitation of the suspension or colloid take place. Kruyt<sup>2</sup> showed that a complete discharge of the suspended particles by the ions of the electrolyte is not necessary for precipitation, as had been supposed, and Powis<sup>3</sup> found that precipitation occurs when the charge is diminished to a certain critical value. According to the Hardy-Schulze law: *the most effective precipitants are ions having a charge of opposite sign to that carried by the suspended particle, the precipitating action being greater the higher their valence (i.e., the greater the number of unit charges carried by the ion)*. It has been found, however, that the coagulation of a suspensoid does not depend solely upon the charge of the ions, but also upon the adsorbability of the ions by the suspended particles. Indeed, as Bancroft<sup>4</sup> pointed out, the Hardy-Schulze law cannot be regarded as more than a guide, and that "since we are dealing with selective adsorption we shall expect to find that some univalent ions will be adsorbed by some substances more than some bivalent or trivalent ions."

**The Velocity of Electrophoresis.** The velocity with which a suspended particle moves through a liquid towards either electrode is readily calculated. In order to make the calculation, let us imagine a particle to be stationary in a cylindrical tube and the liquid to be moving past it. Then, by combining equation 2 with equation 4, it is evident that the velocity with which the liquid moves past the particle is given by the expression:

$$u = \frac{\epsilon \cdot \zeta \cdot E}{4\pi\eta l} \quad (8)$$

This velocity is independent of the radius of the tube. If, now, the liquid is considered as stationary and the particle as moving, obviously the particle must move with the same velocity.

<sup>1</sup> Schoucroum, *J. phys. et radium*, **1**, 65 (1920).

<sup>2</sup> *Verslag Akad. Wetenschappen Amsterdam*, **23**, 260 (1914).

<sup>3</sup> *Z. physik. Chem.*, **89**, 186 (1914).

<sup>4</sup> *J. Phys. Chem.*, **19**, 363 (1915); *Trans. Am. Electrochem. Soc.*, **27**, 175 (1915).

**Measurement of Electrophoresis.** (a) *The Microscopic Method.* This method, which has been most widely employed<sup>1</sup> in the direct measurement of electrophoresis, has the advantage of (a) rapidity, (b) causing no appreciable change in the environment of the particle, (c) permitting the simultaneous determination of differences in the mobility of the particles, (d) high magnification, and (e) of allowing the shape and size of the particles to be observed. Considerable attention has been given to the design of the microelectrophoresis cell, and many improvements have been made. Those employed at the present time are usually of the flat type (Fig. 57<sup>2</sup>), the ratio of the width to the thickness of the cell

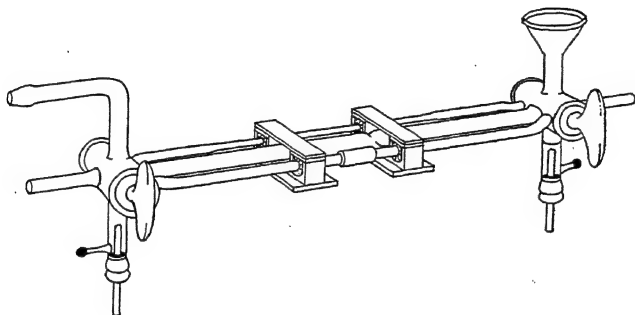


FIG. 57.

being large so that the observed velocity of the particle need not be corrected for electro-osmotic flow of the liquid along the walls.<sup>3</sup> The principles of these cells have been discussed by Thompson.<sup>4</sup>

Among the early measurements of the electrophoretic mobility of particles are those of Burton<sup>5</sup> given in Table XLVI. Microscopic measurements of the velocity of electrophoresis of emulsions of water and aqueous solutions in aniline, guaiacol, and benzonitrile were made by Gyemant.<sup>6</sup> In guaiacol, drops of water and aqueous solutions of inorganic salts

<sup>1</sup> Cf. Ellis, *Z. physik. Chem.*, **78**, 321 (1912); Northrop and Kunitz, *J. Gen. Physiol.*, **7**, 729 (1925); Abramson, *ibid.*, **12**, 469 (1929); **13**, 567 (1930); Abramson and Grossman, *ibid.*, **14**, 563 (1931). For details of technique, see also Mattson, *J. Phys. Chem.*, **32**, 1532 (1928); Hazel and Ayres, *ibid.*, **35**, 2930 (1931); Abramson, *Electrokinetic Phenomena*, Chapter 3; Moyer and Abramson, *J. Gen. Physiol.*, **19**, 727 (1936); Moyer, *J. Bact.*, **31**, 531 (1936).

<sup>2</sup> Northrop and Kunitz, *loc. cit.*

<sup>3</sup> Komagala, *Researches Electrotech. Lab. Tokyo*, **1933**, No. 348.

<sup>4</sup> *Trans. Electrochem. Soc.*, **81**, 147 (1942).

<sup>5</sup> *Phil. Mag.*, **11**, 425 (1906).

<sup>6</sup> *Z. physik. Chem.*, **102**, 74 (1922).

TABLE XLVI  
VELOCITY OF ELECTROPHORESIS

Particle	Velocity towards Anode Under Unit Potential Gradient cm/sec	
	In Water. $\epsilon = 81$	In Ethyl Malonate. $\epsilon = 10.7$
Pt	$20.3 \times 10^{-5}$	$2.3 \times 10^{-5}$
Au	$21.6 \times 10^{-5}$	$1.7 \times 10^{-5}$
Ag	$23.6 \times 10^{-5}$	$1.4 \times 10^{-5}$

migrated slowly or not at all, but drops of solutions containing organic ions exhibited a considerable velocity of electrophoresis. This behavior

was observed to a lesser extent in aniline and still less in benzonitrile. The direction of migration indicated that the drops were negatively charged in the presence of organic cations and positively charged in the presence of organic anions. This behavior is illustrated by the data given in Table XLVII.

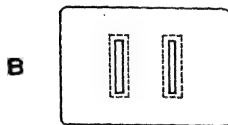
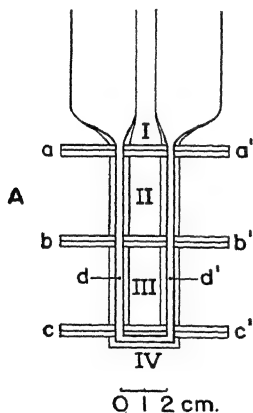


FIG. 58.

(b) *The Moving-Boundary Method.* Although this method had been employed to study electrophoretic movement as early as 1906, it was not until a quarter of a century later that the technique was extraordinarily improved by Tiselius.<sup>1</sup> As a result of these improvements, the moving-boundary method has become a most valuable biological tool for studying proteins and related substances.

The cell used by Tiselius is shown in cross section in Fig. 58, and the complete apparatus is represented in Fig. 59. Sharp initial boundaries are formed in this cell by employing a "shear" technique. The sections I, II, III, and IV (Fig. 58) are capable of sliding over one another.

The initial boundary is produced by filling the U-shaped channel with

<sup>1</sup> *Thesis*, Upsala, 1930; *Trans. Faraday Soc.*, **33**, 524 (1937).

the buffered solution of the material to be studied to a level slightly above *b-b'*. Section II is then pushed to one side and, after removing the excess solution and washing, it is filled with the buffer. On sliding this section back to its original position a sharp boundary is formed.

TABLE XLVII

VELOCITY OF ELECTROPHORESIS OF AQUEOUS EMULSIONS IN GUAIACOL

Potential Gradient = 33 Volts per Cm		
Electrolyte	Velocity in Cm. per Second	Sign of Charge
KCl	Practically zero	Negative Negative Positive
AlCl <sub>3</sub>	Practically zero	
Strychnine nitrate	$2.3 \times 10^{-3}$	
Methylene blue	$20.0 \times 10^{-3}$	
Sodium picrate	$2.6 \times 10^{-3}$	

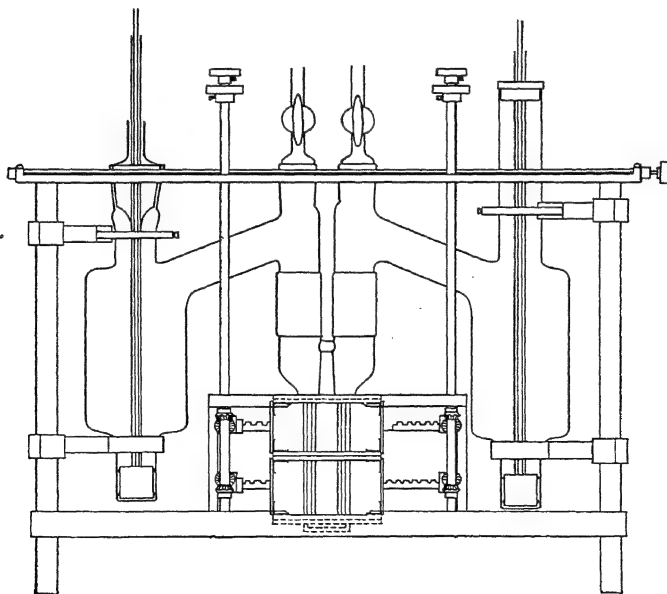


FIG. 59.



Finally, the rest of the apparatus is filled with the buffer. By adapting Toepler's "schlieren" (shadow) method, depending on the refractive index gradient at the boundary, direct visual observation of the boundary is possible during the experiment.<sup>1</sup>

The results obtained by the moving-boundary method in electrophoretic measurements are in good agreement with those obtained by the microscopic method. This is indicated by the data in Table XLVIII.<sup>2</sup>

TABLE XLVIII

COMPARABLE MOBILITIES (mm per sec  $\times 10^{-8}$ ) OF RED BLOOD CELLS  
FOUND BY DIFFERENT OBSERVERS

Method	Rat	Rabbit	Mouse	Guinea Pig
Microscopic	1.45	0.60	1.42	1.16
Moving-boundary	1.45	0.50	1.35	1.11

**Applications of Electro-Osmosis and Electrophoresis.** One of the most important characteristics of the Tiselius apparatus is that it makes possible the separation of a mixture into its components, provided that the particles of these components have different velocities of electrophoresis. For example, many protein mixtures have been separated in this way or the concentrations of the components have been deduced.<sup>3</sup> By this means proteins supposedly simple have been shown to be mixtures, and a separation has been accomplished. The fact that "there are striking and significant differences in the 'electrophoretic patterns' of normal and pathological blood sera, both in the concentrations and in the nature of the constituents," suggests that this method of studying protein solutions may prove of great value.

Electrokinetic studies of solid-organic liquid interfaces have indicated that these may yield valuable information regarding the molecular structure of organic compounds.<sup>4</sup>

The possibility of the commercial utilization of electrokinetic processes

<sup>1</sup> For a detailed account of the Tiselius apparatus and its operation, see Longworth and MacInnes, *Chem. Revs.*, **24**, 271 (1939); MacInnes, *Science in Progress*, p. 214, 1940. A modification of the schlieren method is described by Longworth, *J. Am. Chem. Soc.*, **61**, 529 (1939).

<sup>2</sup> Abramson, *Trans. Faraday Soc.*, **35**, 7 (1940).

<sup>3</sup> Cf. Longworth, *J. Am. Chem. Soc.*, **61**, 529 (1939); Longworth and MacInnes, *ibid.*, **62**, 705 (1940); Longworth, *Ann. N. Y. Acad. Sci.*, **41**, 267 (1941); *Chem. Revs.*, **30**, 323 (1942); Longworth and MacInnes, *J. Gen. Physiol.*, **25**, 507 (1942); van Dyke, Chow, Greep, and Rothen, *J. Pharmacol.*, **74**, 190 (1942); Abramson, Moore, and Gettner, *J. Phys. Chem.*, **46**, 192 (1942).

<sup>4</sup> Gortner, *Trans. Faraday Soc.*, **35**, 63 (1940).

has received considerable attention.<sup>1</sup> Nevertheless there still remains much investigation to be carried out in this field. Up to the present time there has been a large-scale adoption of but few of the applications that have been proposed, probably owing to a lack of knowledge of the conditions necessary for securing the best results.

The first two applications of electro-osmosis appear to be the electric *tanning of leather*<sup>2</sup> and the drying of wood. In the former process, the tan-liquor is carried into the skins by electro-osmosis. A disadvantage of this process is the occurrence of oxidation of tannin at the anode.

As early as 1900 Count Schwerin was granted a patent for removing *water from peat* by electro-osmosis. The wet peat was placed between a suitable anode and a perforated cathode. When a current was passed through the peat, the water migrated to the cathode and escaped through the perforations. Although this process has received a great deal of consideration, it has been possible to decrease the water content of peat to only about 65 per cent. With a potential difference of 4–5 volts between the electrodes, the electrical energy required to reduce the water in 1000 kg of peat from 90 to 65 per cent amounts to 130 kilowatt-hours. Since a very large percentage of the water is *adsorbed*, the difficulty, as Briggs points out, "lies in the removal of this adsorbed moisture; only water held *mechanically* can be removed by electrokinetic processes."

A successful technical application of electrophoresis is found in an electrolytic process for *waterproofing textile fabrics*.<sup>3</sup> In this process finely divided alumina or aluminum hydroxide is carried into the interstices of the fabric by electrophoresis. In the electrical industries and in the field of surface protection there has been rapid progress in the technical application of electrokinetics. The electrophoretic deposition of insulating materials in the radio-valve industry has been described.<sup>4</sup> This method has also been employed<sup>5</sup> successfully to lacquer tin cans internally, effecting thereby an economy in volatile thinners; and it has

<sup>1</sup> Cf. W. C. McC. Lewis, *J. Soc. Chem. Ind.*, **35**, 575 (1916); Kruyt, *Chem. Weekblad*, **14**, 766 (1917); Briggs, *Rept. Brit. Assoc. Advancement Sci.*, **1918**, "Report on Colloidal Chemistry," pp. 39–52 (this paper gives an excellent bibliography of the patent literature); Highfield, Ormandy, and Northall-Lawrie, *Pottery Gaz.*, **45**, 775 (1920); Ormandy, *Chem. Age* (London), **3**, 475 (1920); Frausnitz, *Z. Elektrochem.*, **28**, 27 (1922); Bary, *Chimie & industrie*, **7**, 640 (1922), *Chem. Trade J.*, **70**, 625 (1922) — a review with bibliography; Frydlander, *Rev. prod. chim.*, **25**, 721 (1922).

<sup>2</sup> Cf. Buse, *J. Soc. Chem. Ind.*, **19**, 59 (1900); Rideal and Evans, *ibid.*, **32**, 633 (1913); Williams, *J. Am. Leather Chem. Assoc.*, **8**, 328 (1913).

<sup>3</sup> Cf. Creighton, *J. Franklin Inst.*, **192**, 497 (1921).

<sup>4</sup> Benjamin and Osborn, *Trans. Faraday Soc.*, **35**, 287 (1940).

<sup>5</sup> Sumner, *ibid.*, **35**, 272 (1940).

proved successful in the deposition of coatings of synthetic resins on metals.<sup>1</sup> The problem of dewatering clay by electrokinetic methods has been considered and studied.<sup>2</sup>

Among other applications of electrokinetic processes that have been used or proposed, the following may be mentioned: the dehydration of coloring matters and finely divided stearate; the purification of glues, gelatine, crude glycerol, fruit juices, nitrocellulose, alkaloids, and serums; the extraction of sugar from beets and molasses; the preparation of silica gels from sodium silicate; the separation of oil-water emulsions in the petroleum industry; the fractionation of suspended colloids; the decolorization of liquids; the concentration of radioactive substances; the plating of rubber and the infiltration of drugs.

**Streaming Potential.** It was first pointed out by Quincke<sup>3</sup> that there should be a potential difference between the two sides of a porous diaphragm when a liquid is forced through its pores; and that when a liquid flows through a capillary tube a potential difference should exist between its ends. This phenomenon is the reverse of electro-osmosis. A potential difference established in this manner is called a **streaming potential**, and it is related to the  $\zeta$  potential as follows:

$$E = \frac{\zeta P \epsilon}{4\pi \eta \kappa} \quad (9)$$

In this expression  $\eta$  and  $\kappa$  are the viscosity and the specific conductance, respectively, of the liquid,  $P$  is the hydrostatic pressure causing the flow, and the other quantities have their usual meaning. Due to the same cause, an electric current is generated when fine solid particles fall through a liquid.

Numerous measurements have been made of streaming potentials, since these afford a very convenient means of studying electrokinetic phenomena and of determining  $\zeta$  potentials.<sup>4</sup> The streaming-potential technique has been largely developed by Gortner and his co-workers,<sup>5</sup>

<sup>1</sup> Gemant, *Ind. Eng. Chem.*, **31**, 1233 (1933); Genin, *Rev. gén. élec.*, **47**, 391 (1940).

<sup>2</sup> Curtis, *Trans. Electrochem. Soc.*, **73**, 503 (1938); Thompson and Speil, *ibid.*, **81**, 119 (1942).

<sup>3</sup> Pogg. Ann., **107**, 1 (1859).

<sup>4</sup> Krut, *Kolloid Z.*, **22**, 81 (1918); Freundlich and Rona, *Preusz. Akad. Wiss.*, **20**, 397 (1920); Freundlich and Ettisch, *Z. physik. Chem.*, **116**, 401 (1925); Krut and van der Willigen, *Kolloid Z.*, **45**, 307 (1928); Gortner and co-workers, see numerous papers in the *J. Phys. Chem.*, between 1930 and 1938; Gortner, *Trans. Faraday Soc.*, **35**, 63 (1940).

<sup>5</sup> *Loc. cit.* For a description of the streaming-potential apparatus employed see Lauffer and Gortner, *J. Phys. Chem.*, **34**, 1509 (1930); Martin and Gortner, *ibid.*, **42**, 641 (1938).

who have found it to be admirably adapted to the study of colloidal behavior.

**Electrostenolysis.** Closely related to electro-osmosis is the phenomenon of electrostenolysis, which was first observed by Braun.<sup>1</sup> He found that, when a solution of a salt, separated into two portions by a capillary tube, was electrolyzed, a deposition of metal or an evolution of gas took place in the capillary tube. According to Coehn<sup>2</sup> the wall of the capillary becomes negatively charged, owing to electro-osmosis, and, in consequence, positively charged metal ions are attracted to and discharged on the wall of the tube.

### REFERENCES

- ABRAMSON, *Electrokinetic Phenomena and Their Applications*, 1934.  
"Symposium on the Electrical Double Layer," *Trans. Faraday Soc.*, **35**, 1-322 (1940).  
ABRAMSON, MOYER, and GORIN, *Electrophoresis of Proteins*, 1943.

### PROBLEMS<sup>3</sup>

1. The potential of the electric double layer formed by glass and water is 0.050 volt. Calculate the volume of water which would flow past a fixed point in a tube having a diameter of 0.0376 cm, in 1 hour, when there is a potential difference of 154 volts between the electrodes which are 10 cm. apart. (The viscosity of water may be taken as 0.0105, and its dielectric constant as 81.)

2. Very fine particles of glass are suspended in water placed between electrodes which are 20 cm. apart. Given that the potential difference between the electrodes is 40 volts, that the potential between the glass particles and the water is 0.050 volt, and that the dielectric constant and the viscosity of water are 81 and 0.0105, respectively, calculate the velocity with which the glass particles move towards the anode.

3. It has been found that, when particles of quartz having a diameter of 0.001 mm are suspended in water, the potential of the electric double layer is 0.032 volt. Calculate the velocity of cataphoresis of the particles towards the anode, under a potential gradient of 3 volts per centimeter.

4. A capillary U-tube having a uniform diameter of 0.0738 cm is partly filled with water. From data given in the preceding problems, calculate the maximum difference that may be obtained between the levels of the liquid in the two arms of the tube, when the potential difference between the electrodes is 5120 volts.

<sup>1</sup> *Wied. Ann.*, **42**, 450 (1891); **44**, 473 (1891).

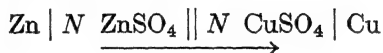
<sup>2</sup> *Z. physik. Chem.*, **25**, 651 (1898); *Z. Elektrochem.*, **4**, 501 (1898).

<sup>3</sup> In solving these problems, it must be remembered that all quantities must be expressed in absolute units (see p. 157).

## CHAPTER VIII

### ELECTROMOTIVE FORCE

**Voltaic Cells.** In a voltaic cell, chemical energy is transformed into electrical energy. In the Daniell cell,



electrical energy results from the reaction:



whereby zinc is dissolved from the zinc electrode and copper is simultaneously deposited on the copper electrode, and the concentration of the copper sulphate is diminished. In order that the electromotive force of this cell remain constant, the concentration of the copper sulphate must be kept constant. If a voltaic cell is to produce a continuous current, it is essential that positive ions enter solution and, simultaneously, an equivalent quantity of negative ions leave the solution.<sup>1</sup>

In the diagrammatic representation of voltaic cells, we shall sometimes employ a long arrow to indicate the direction of the flow of *positive* electricity *inside* the cell. The arrow, therefore, will point towards the positive pole of the cell. In the above representation of the Daniell cell, positive electricity flows inside the cell from the negative zinc pole to the positive copper pole.

**The Measurement of Electromotive Force.** When the poles of a voltaic cell are joined by a wire, there is a fall of potential and a flow of current in the wire. This fall of potential, as we have seen (equation 2, Chapter I), is equal to the electromotive force of the cell, when the resistance of the wire is large in comparison with the internal resistance of the cell. When first one voltaic cell and then another is connected in series with a sensitive galvanometer, through a high resistance, the deflection ( $D$ ) of the galvanometer is proportional to the strength of the current ( $I$ ) which each cell sends through the circuit. If the internal resistances of the two cells are negligible in comparison with the external resistance, we may write

<sup>1</sup> Cf. Ostwald, *Phil. Mag.*, **32**, 145 (1891).

$$I = \frac{E}{R_{ex}} \quad (1)$$

from which it follows that

$$\frac{I_1}{I_2} = \frac{D_1}{D_2} = \frac{E_1}{E_2}$$

or

$$E_1 = E_2 \frac{D_1}{D_2} \quad (2)$$

Provided, therefore, that the electromotive force of one of the cells is known, that of the other can be calculated.

When the internal resistance of a cell is not negligible in comparison with the external resistance, the electromotive force of the unknown cell may be determined by placing the two cells in the same circuit with the galvanometer; first in series and then opposed to one another. If we represent the electromotive force of the known, or **normal**, cell and that of the unknown cell by  $E_n$  and  $E_x$ , respectively, and their internal resistances by  $R'_{in}$  and  $R''_{in}$ , then the current which flows through the galvanometer when the cells are placed in series is given by the expression

$$\begin{aligned} I_1 &= \frac{E_x}{R_{ex} + R'_{in} + R''_{in}} + \frac{E_n}{R_{ex} + R'_{in} + R''_{in}} \\ &= \frac{E_x + E_n}{R_{ex} + R'_{in} + R''_{in}} \end{aligned} \quad (3)$$

and when the cells are opposed to one another, by the expression

$$\begin{aligned} I_2 &= \frac{E_x}{R_{ex} + R'_{in} + R''_{in}} - \frac{E_n}{R_{ex} + R'_{in} + R''_{in}} \\ &= \frac{E_x - E_n}{R_{ex} + R'_{in} + R''_{in}} \end{aligned} \quad (4)$$

By combining equations 3 and 4, we obtain

$$\frac{I_1}{I_2} = \frac{E_x + E_n}{E_x - E_n}$$

or

$$E_x = E_n \frac{I_1 + I_2}{I_1 - I_2} \quad (5)$$

Since  $I_1$  and  $I_2$  are proportional to the deflections of the galvanometer the electromotive force of the unknown cell may be calculated readily.

**The Poggendorff Compensation Method.** The electromotive force of a cell is most conveniently determined by measuring the potential difference between its poles *when the circuit is open*, that is, when the external resistance is infinitely large. This may be done by the Poggendorff compensation method. In this method, the electromotive force of the unknown cell is exactly compensated by that of another cell—called a *working cell*—of constant electromotive force, preferably a storage cell (see p. 268). The working cell *S* is connected to the ends, *A* and *C*, of

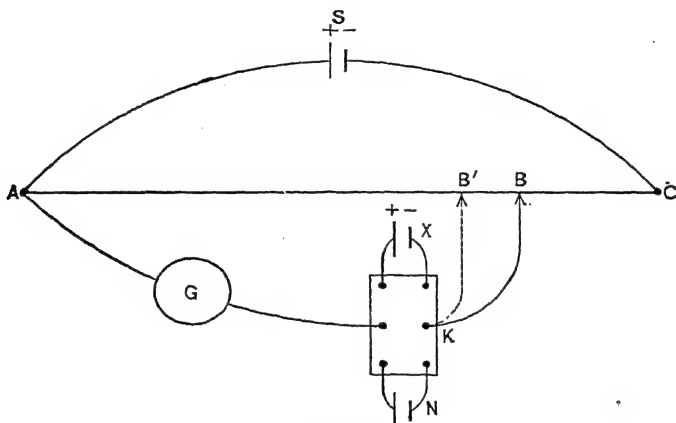


FIG. 60.

the slide wire of a Wheatstone bridge, as shown in Fig. 60. The unknown cell *X*, and a normal cell *N*, are connected to a double-pole, double-throw switch *K*. One of the middle poles of *K* is connected through an electrometer or sensitive galvanometer *G* to one of the ends of the bridge wire, while the other pole is joined to the sliding contact *B* of the bridge wire. The switch *K* is then closed so as to place the unknown cell in the circuit, and the sliding contact moved along the bridge wire, in one direction or the other, until a position, *B*, is found at which no current flows through *G*. The normal cell is then placed in the circuit by throwing *K* in the opposite direction, and a second position, *B'*, is found at which no current flows through *G*. Since

$$\frac{E_n}{E_x} = \frac{AB'}{AB}$$

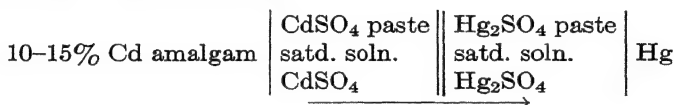
or

$$E_x = E_n \frac{AB}{AB'} \quad (6)$$

the electromotive force of the unknown cell may be calculated. In accurate measurements of electromotive force, the slide-wire bridge is replaced by a potentiometer.

It has been difficult to measure the electromotive force of cells having a high internal resistance, owing to the lack of sufficient amperage to actuate the galvanometer. Beans and Oakes<sup>1</sup> devised a method which overcomes this difficulty. In this method a condenser of adequate capacity is charged with electricity, first from the cell under investigation and then from a normal cell. In each case the condenser is discharged through a calibrated ballistic galvanometer. In this way, the electromotive force of high-resistance cells may be determined with an accuracy of 0.5 millivolt.

**Normal or Standard Cells.** The standard cell which is almost universally used in the measurement of electromotive force is the **Weston or cadmium cell**. This consists of:



The now accepted value of the electromotive force of this cell, when made in accordance with the proper specifications, is 1.01827 volts at 20°.<sup>2</sup> Its electromotive force at any temperature between 0° and 40° is given by the expression:

$$E_t = E_{20} - 0.0000406(t - 20) - 9.5 \cdot 10^{-7}(t - 20)^2 + 10^{-8}(t - 20)^3 \quad (7)$$

This expression shows that the temperature coefficient of the electromotive force of the Weston cell is nearly zero. On account of this and its constancy, this cell is the most widely employed standard in electromotive-force measurements. The effects of aging are small and amount to but a few microvolts per annum. The constancy of the cell has been studied by several investigators.<sup>3</sup> The electromotive force of the Weston cell is practically independent of the pressure. It has been found<sup>4</sup> that a pressure of 12,000 atmospheres increases it only about 5 per cent.

<sup>1</sup> *J. Am. Chem. Soc.*, **42**, 2116 (1920).

<sup>2</sup> Rosa and Vinal, *Proc. Natl. Acad. Sci. U. S.*, **3**, 59 (1917).

<sup>3</sup> Cf. Vosburgh and Elmore, *J. Am. Chem. Soc.*, **53**, 2819 (1931); Vinal and Howard, *Bur. Standards J. Research*, **11**, 255 (1933). A detailed procedure for the maintenance of the standard emf within 1-2 parts per million is given by Shaw and Reilley, *Can. J. Research*, **3**, 473 (1930); the care of the cell has been discussed by Eppley, *Elec. Eng.*, **51**, 341 (1932).

<sup>4</sup> Poulter and Carter, *Phys. Rev.*, **39**, 816 (1932).



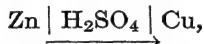
A standard cell having a low temperature coefficient has been prepared<sup>1</sup> by substituting cadmium-bismuth amalgam for the cadmium amalgam in the Weston cell, and saturating the electrolyte with both  $\text{CdSO}_4 \cdot \text{Na}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$  and  $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ . The electromotive force of this cell is 1.0184 volt at 25°, and its temperature coefficient is 0.000013 volt per degree.

A low voltage standard cell was prepared by Oblata.<sup>2</sup> This cell



gives a constant electromotive force of 0.09838 volt at 20°.

**Reversible and Non-Reversible Cells.** When 1 faraday of electricity is produced by a Daniell cell, one equivalent of zinc goes into solution at the anode and a like quantity of copper deposits at the cathode. If, now, the direction of the current is reversed by applying an external electromotive force and the same quantity of electricity is forced through the cell from the copper to the zinc, the cell will return to its original condition. Such a cell is called a **non-polarizable** or a **reversible cell**.<sup>3</sup> On the other hand, when 1 faraday is developed by the cell,

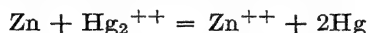


one equivalent of zinc goes into solution and one equivalent of hydrogen is liberated at the copper electrode. If the same quantity of electricity is then passed through the cell in the opposite direction, one equivalent of copper will go into solution and a like quantity of hydrogen will be set free at the zinc electrode. Thus the reversal of the current does not bring this cell back to its original condition. A cell of this kind is called a **polarizable** or **non-reversible cell**. In general a **reversible electrode** is formed when a metal that is not too negative is partially immersed in a saturated solution of its own ions. The Daniell cell is composed of two reversible electrodes. Below are described a few types of reversible voltaic cells.

(a) *Chemical cells*, in which a chemical reaction is involved, e.g.,



in which electrical energy results from the reaction

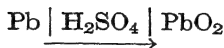


<sup>1</sup> Vosburgh, Guagenty, and Clayton, *J. Am. Chem. Soc.*, **59**, 1256 (1937).

<sup>2</sup> *Proc. Phys. Math. Soc. Japan*, **3**, 136 (1921).

<sup>3</sup> No cell is strictly non-polarizable. The term implies that it cannot be polarized even by considerable currents. Many cells, however, are reversible in the thermodynamic sense, provided that only small currents are used.

and (ii)

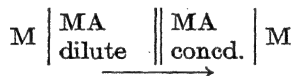


in which the following reaction takes place:



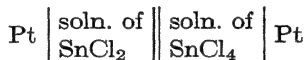
(This reaction will be discussed in detail in Chapter XI.) When an electric current is sent through these cells in the opposite direction to that represented by the arrow, the reactions represented by the above equations take place from right to left.

(b) *Concentration cells* are voltaic cells which make use of the "dilution tendency" of dissolved substances. Cells of this type are formed when, for example, electrodes of the same metal dip into solutions containing ions of the metal at different concentrations, e.g.,



In these cells the production of electrical energy results from changes in the concentrations of the electrolyte.

(c) *Oxidation-reduction cells.* A reversible cell is formed when platinum electrodes dip into solutions of oxidizing and reducing agents, e.g.,



Among other types of reversible voltaic cells may be mentioned the following: cells comprised of allotropic forms of the same metal, cells containing a stable and unstable salt of a metal (e.g.,  $\text{Na}_2\text{SO}_4$  and  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ), and photoelectric cells.

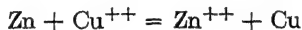
**The Relation between Chemical and Electrical Energy.** It was pointed out in Chapter I that different forms of energy may be transformed into one another. For example, electrical energy may be produced from mechanical energy by means of a dynamo, from thermal energy with the aid of a thermopile, and from chemical energy by means of a voltaic cell. It should be possible, therefore, to derive a relation between the electrical energy, or external work (since the electrical energy can be directly utilized to produce work, e.g., by an electric motor), produced by a voltaic cell and the chemical energy expended in its production.

The chemical energy of a process (reaction) is equal to the heat effects of the process, that is, to the heat of reaction,  $q$ , when the process

takes place without the performance of external work. This is the case when the volume change is negligible. Long ago, it was believed that when a chemical reaction takes place in a voltaic cell the electrical energy produced is equal to the heat of the reaction; i.e.,

$$zFE = q \quad (8)$$

where  $E$  is the electromotive force of the cell and  $q$  is the number of calories developed by the interaction of  $z$  equivalents of the reactants. This relation is known as the Helmholtz-Thomson rule. Since at  $0^\circ$  the heat of the reaction



is 50,110 calories, in accordance with this rule the electrical energy produced when the reaction takes place in a voltaic cell should be  $50,110 \times 4.182 = 209,560$  joules. Since the experimental value of the electromotive force of the Daniell cell at  $0^\circ$  is 1.096 volts, the electrical energy actually developed is  $zFE = 2 \times 96,500 \times 1.096 = 211,528$  joules. Although for this cell the Helmholtz-Thomson rule is approximately correct, the difference between observation and calculation is considerably greater for many other cells. Thorough experimental investigation has long since shown <sup>1</sup> that in a voltaic cell the chemical energy is usually only *partially* transformed into electrical energy.

In accordance with the first law of thermodynamics, or the principle of the conservation of energy, the *decrease in the total energy* ( $U$ ) of a voltaic cell is equal to the sum of the electrical energy or work and the heat developed by the cell. Expressed mathematically,

$$U = A - Q \quad (9)$$

where  $A$  is the work produced and  $Q$  is the heat *absorbed* by the cell. This equation shows that when  $A$  is greater than  $U$  the cell absorbs heat from the surroundings and changes it into electrical energy; when  $A$  is less than  $U$  not all the chemical energy is transformed into electrical energy. Since the decrease in total energy of a system depends only on its initial and final states, it follows that at the same temperature the decrease in the total energy of a process taking place in a voltaic cell is equal to the heat of reaction <sup>2</sup> of the process when it takes place *outside* the cell, i.e.,

$$U = -q \quad (10)$$

<sup>1</sup> Cf. Thomson, *Wied. Ann.*, 11, 246 (1880); Braun, *ibid.*, 17, 593 (1882).

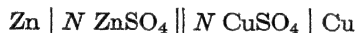
<sup>2</sup> Following the custom of thermodynamics, heat *developed* by a reaction is taken as *negative*.

An important and exact relation between electrical and chemical energy may be derived by means of the well-known Gibbs-Helmholz equation

$$A - U = T \frac{dA}{dT} \quad (11)$$

where  $A$  is the maximum work done by a process,  $U$  is the decrease in the total energy of the system in which the process takes place, and  $T$  is the absolute temperature. It may be pointed out here that a process yields the maximum available work only when it is carried out *reversibly*, that is, when it is operated under equilibrium conditions. Accordingly, a voltaic cell produces the maximum electrical energy only when a very feeble current is allowed to flow, since otherwise the equilibrium between the substances in the cell is disturbed and it ceases to operate reversibly.

Let us now consider the energy changes which occur in a reversible voltaic cell, e.g.,



having an electromotive force  $E$  at an absolute temperature  $T$ . When this cell develops electrical energy, the reaction



takes place. The heat of this reaction is equal to the decrease in the total energy which occurs in the cell.

Now allow the cell to produce electrical energy (under reversible conditions) for as long as it takes 1 gram atom of zinc to enter solution and 1 gram atom of copper to deposit on the copper electrode. The maximum work available is

$$A = zFE$$

where  $z$  is the valence of the metals. On differentiating  $A$  we get

$$dA = zFdE$$

and on substituting this value of  $dA$ , together with those of  $A$  and  $U$  (equation 10), in equation 11, we obtain:

$$zFE + q = T \frac{zFdE}{dT}$$

whence

$$E = \frac{-q}{zF} + T \frac{dE}{dT} \quad (12)$$

If  $E$  is expressed in volts and  $q$  in calories, then

$$E = \frac{-Jq}{zF} + T \frac{dE}{dT} \quad (12a)$$

where  $J$  is the electrical equivalent of heat. It will be observed that, when  $dE/dT$  is positive, the electromotive force of a reversible voltaic cell increases with rise in temperature; when  $dE/dT$  is negative the reverse holds; when the temperature coefficient is zero, the electrical energy is equal to the chemical energy and the Helmholtz-Thomson rule is valid. (The smaller the temperature coefficient, the more nearly does the rule hold.) If the temperature coefficient is positive, a quantity of

heat,  $Q = zT \frac{dE}{dT}$  per faraday, must be added to the cell in order to maintain it at a constant temperature,  $T$ . On the other hand, if the temperature coefficient is negative, the temperature of the cell remains constant only when the same quantity of heat is withdrawn from the cell.

Equation 12 was first derived by Helmholtz and later tested qualitatively by Czapski<sup>1</sup> and quantitatively by Jahn,<sup>2</sup> Bugarszky<sup>3</sup> and Cohen, Chattaway and Tombrok.<sup>4</sup> For the Daniell cell at 15°, the last-named investigators found that  $E = 1.09337$  volts and  $dE/dT = -0.000429$  volt. Accordingly, from equation 12a,

$$\begin{aligned} q &= \frac{-2 \times 96,500}{4.182} (1.09337 + 288 \times 0.000429) \\ &= -56,160 \text{ calories} \end{aligned}$$

whereas the value of the heat of reaction as determined by experiment is  $-55,189$  calories. Some of the results obtained by Jahn and by Bugarszky are given in Table XLIX. The last cell given in the table affords an example of an endothermic reaction that is electromotively active.

The results that have been given show that heats of reaction may be determined by electromotive force measurements. If the heat of formation of one of the compounds in the cell is known, then that of the other may be calculated from the heat of the reaction which takes place in the cell. In this way, for example, Getman<sup>5</sup> determined the heat of forma-

<sup>1</sup> *Wied. Ann.*, **21**, 209 (1884).

<sup>2</sup> *Ibid.*, **50**, 189 (1893).

<sup>3</sup> *Z. anorg. Chem.*, **14**, 145 (1897).

<sup>4</sup> *Z. physik. Chem.*, **60**, 706 (1907).

<sup>5</sup> *J. Am. Chem. Soc.*, **40**, 11 (1918).

tion of lead chloride, Krahmer <sup>1</sup> that of silver bromide, Oblata <sup>2</sup> that of cadmium iodide, and Jones and Schumb <sup>3</sup> the heat of formation of thal-  
lous iodide. By this method, Taylor and Anderson <sup>4</sup> obtained the value  
-15,134 calories, and Gerth <sup>5</sup> the value -15,150 calories for the heat  
of formation of silver iodide.

TABLE XLIX  
EXPERIMENTAL VERIFICATION OF HELMHOLTZ'S EQUATION

Cell	$E$ at 0° Volts	$\frac{dE}{dT}$	$q$ in Calories	
			Obs.	Calcd.
$\text{Pb} \mid \text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \parallel \text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 + \text{aq} \mid \text{Cu}$ $+ 100\text{H}_2\text{O}$	0.470	+0.000385	-17.532	-16.900
$\text{Zn} \mid \text{ZnCl}_2 + 100\text{H}_2\text{O} \parallel \text{AgCl} \mid \text{Ag}$	1.015	-0.000402	-52.046	-51.989
$\text{Zn} \mid \text{ZnBr}_2 + 25\text{H}_2\text{O} \parallel \text{AgBr} \mid \text{Ag}$	0.828	-0.000106	-39.762	-39.602
$\text{Hg} \mid \frac{\text{Hg}_2\text{O in}}{0.01 \text{ N KOH}} \parallel \frac{1.0 \text{ N KNO}_3}{\text{H}_2\text{Cl}_2 \text{ in}} \mid \text{Hg}$ $0.01 \text{ N KCl}$	0.1483 ( $t = 18.5$ )	+0.000837	+ 3.280	+ 3.710

The Gibbs-Helmholtz equation may be used to determine the theoretical voltage of a cell in the calculation of "energy efficiency" (see Chapter II).

**Electrolytic Solution Pressure.** It is well known that the vapor pressure of a liquid or a solid is a measure of its tendency to assume the gaseous state. On account of the analogy between dissolved substances and gases, the tendency of a substance to enter solution may be termed its **solution pressure**. In the case of metals immersed in water (or other liquids), Nernst <sup>6</sup> assumed that there exists a definite tendency to pass from the atomic to the ionic state, and this tendency he designated as **electrolytic solution pressure (P)**. Numerical values of electrolytic solution pressure, calculated from electromotive force data, vary from the infinite to the infinitesimal, as is shown by Table L. In general these values decrease in the same order as the electropositive character of the metal increases. The non-metals also have been assumed to have electrolytic

<sup>1</sup> *Z. Elektrochem.*, **26**, 97 (1920).

<sup>2</sup> *Proc. Phys. Math. Soc. Japan*, **3**, 136 (1921).

<sup>3</sup> *Proc. Am. Acad. Arts and Sci.*, **56**, 199 (1921).

<sup>4</sup> *J. Am. Chem. Soc.*, **43**, 2014 (1921).

<sup>5</sup> *Z. Elektrochem.*, **27**, 287 (1921).

<sup>6</sup> *Z. physik. Chem.*, **4**, 150 (1889).

solution pressures. The order of these elements with respect to their tendency to pass from the atomic to the ionic state is: F, Cl, Br, I, S.

Owing to the difficulty of attributing any physical significance to electrolytic solution pressure,<sup>1</sup> this concept has met with a great deal of criticism, in spite of its usefulness. For instance, Lehfeltdt<sup>2</sup> showed that, in order to produce the electrolytic solution pressure ascribed to

TABLE L  
ELECTROLYTIC SOLUTION PRESSURES

Metal	Electrolytic Solution Pressure in Atmospheres
Magnesium	$1.1 \times 10^{43}$
Zinc	$9.9 \times 10^{18}$
Cadmium	$2.7 \times 10^6$
Iron	$1.2 \times 10^4$
Cobalt	1.9
Nickel	1.3
Lead	$1.1 \times 10^{-3}$
Hydrogen	$9.9 \times 10^{-4}$
Mercury	$1.1 \times 10^{-16}$
Silver	$2.3 \times 10^{-17}$
Copper	$4.8 \times 10^{-20}$
Paladium	$1.5 \times 10^{-36}$
Platinum	$1 \times 10^{-36}$

zinc, 1.27 grams of the metal would have to assume the ionic state, per square centimeter of metal surface in contact with water. This is not borne out by experiment. Further, this writer stated: "There are certain obvious difficulties in the way of accepting these numbers [see Table L] as representing a physical reality. The first of them is startlingly large; that, however, may not be a true difficulty. The [last] is so small as to involve the rejection of the entire molecular theory of fluids. If it is true that fluids consist of molecules with a diameter of  $10^{-8}$  centimeter, then the production of a pressure so low is impossible; for pressure is a statistical effect due to the impact of numerous molecules." Notwithstanding these and other objections, the conception of electrolytic solution pressure, together with the theory of electrolytic dissociation, has given a deeper insight into the mechanism of the production of potential differences within voltaic cells. Indeed, Butler has

<sup>1</sup> An attempt to visualize the concept of electrolytic solution pressure has been made by Smits, *Proc. Koninkl. Akad. Wetenschappen Amsterdam*, **18**, 1485 (1916). Cf. Heyrovský, *Compt. rend.*, **180**, 1655 (1925).

<sup>2</sup> *Phil. Mag.*, **48**, 430 (1899).

shown,<sup>1</sup> as the result of kinetic considerations, that the concept of electrolytic solution pressure is justifiable.

In accordance with Nernst's assumption, when a bar of, say, zinc is placed in water, zinc atoms each give up two electrons to the bar of metal and pass into the water as positively charged zinc ions. In this way an electric double layer is formed at the junction of the metal and the liquid. That but an exceedingly minute quantity of zinc enters the water in the form of ions, notwithstanding its enormous electrolytic solution pressure, is due to the electrostatic attraction of the negative charges which accumulate on the bar of metal. Equilibrium is so quickly established between these opposing forces that the amount of zinc that enters the water in the form of ions is far too small to be detected analytically. Since the electrolytic solution pressure of copper is infinitesimal, it is evident that the number of negative charges necessary to prevent atoms of this metal from assuming the ionic state must be very much smaller than in zinc. Hence, if a solution of copper sulphate is added to water in which is immersed a piece of zinc, copper ions will discharge and deposit on the zinc. Since thereby the number of negative charges on the zinc is reduced, more zinc atoms are enabled to assume the ionic state. The amount of zinc which enters solution is equivalent to the amount of copper which deposits on the zinc. Similarly, when any metal is immersed in a solution of a salt of a metal having a lower electrolytic solution pressure, the latter metal is deposited and the former enters solution in the form of ions. These considerations afford an explanation of why, for example, copper deposits on a piece of iron that is dipped in a solution of a copper salt, and why certain metals are dissolved by acids and others are not.

**Electrolytic Solution Pressure and Osmotic Pressure.** When a piece of metal having a high electrolytic solution pressure is placed in a solution containing its own ions, the change from the atomic to the ionic state is opposed by both the osmotic pressure ( $P$ ) of the metal ions already in solution, and the electrostatic attraction of the negative charges which accumulate on the metal. On the other hand, when a metal with a very low electrolytic solution pressure, such as silver or copper, is placed in a solution of its ions, the osmotic pressure, which is very much greater than the electrolytic solution pressure, causes some of the ions to deposit on the metal, thereby giving it a positive charge. In this case the amount of metal deposited is far too small to be weighable, for the accumulating positive charges very soon prevent a further deposition of positive ions. Evidently the relative values of the osmotic

<sup>1</sup> *Trans. Faraday Soc.*, **19**, 729 (1924). Cf. Hammerschmid and Lange, *Physik. Z.*, **32**, 958 (1931).



pressure and the electrolytic solution pressure determine whether ions leave or enter solution, when a metal is immersed in a solution containing its own ions. Obviously the following three cases are possible:

1. When

$$P < P$$

ions enter solution, the metal and the solution become negatively and positively charged, respectively, and a potential difference is established between the metal and the solution.

2. When

$$P = P$$

an electric double layer is not formed and, consequently, there is no potential difference between the metal and the solution.

3. When

$$P > P$$

ions leave the solution and the metal becomes positively charged, and the force of the electrostatic repulsion between the metal and the positive

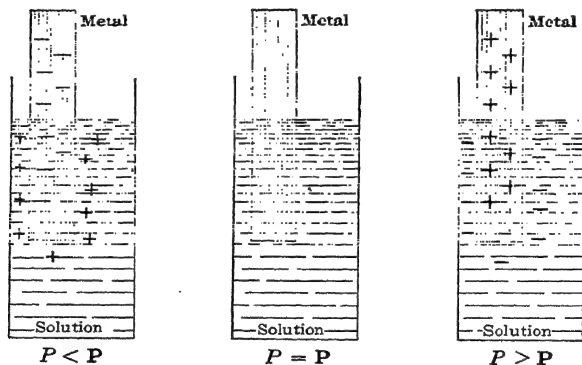


FIG. 61.

ions in solution is superimposed on the electrolytic solution pressure of the metal. As in case 1, a potential difference is established between the metal and the solution, but here it is due to an electric double layer formed by the positive charges on the metal and the negative ions in the solution. The three cases are represented diagrammatically in Fig. 61.

It was first shown by Palmaer<sup>1</sup> that, when a stream of fine drops of mercury is allowed to fall through a solution of a mercurous salt con-

<sup>1</sup> *Z. physik. Chem.*, **25**, 256 (1898); **28**, 257 (1899); **36**, 664 (1901).

tained in a tall vessel (Fig. 62), the bottom of which is covered with mercury, the concentration of the upper portion of the solution decreases and that of the lower portion increases. This phenomenon is readily explained on the basis of Nernst's theory of electrolytic solution pressure. Since  $P > P$ , the droplets of mercury acquire a positive charge on entering the solution and, consequently, negative ions are attracted to the layer of solution at the interface. As the droplets fall to the bottom of the vessel they carry negative ions with them. On reaching the bottom the drops coalesce and, as their surface is thereby greatly diminished, mercurous ions pass into the layer of solution adjacent to the mercury. In this way the concentration of the lower layers increases and that of the upper layers decreases.

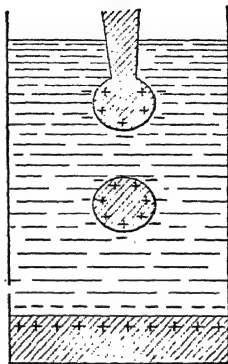


FIG. 62.

**Sign of Electrode Potentials.** In order to indicate the direction of the polarity between a metal and a solution, we shall place before the potential difference between the two phases—the so-called potential of the metal or the electrode potential—the sign of the charge on the metal.<sup>1</sup> In solutions containing their own ions, noble metals (e.g., gold, mercury, silver, copper) acquire a positive potential, whereas base metals (e.g., zinc, aluminum, cadmium, lead, iron, nickel) acquire a negative potential. In accordance with this convention, the potential of a metal in contact with a solution containing its own ions is positive when  $P < P$ , and negative when  $P > P$ .

A short arrow will sometimes be placed above a metal-solution junction to indicate the direction in which the positive current *tends* to flow. When the arrow points *towards* the metal, its potential is *positive*; when it points *away* from it, its potential is *negative*.

<sup>1</sup> This convention, according to Bancroft [*Trans. Am. Electrochem. Soc.*, **33**, 79 (1918)] the only one which can be adopted universally, has been adopted officially by the *Bunsen Gesellschaft*, the *American Electrochemical Society*, and the *Bureau of Standards*, of Washington, and is employed by most European electrochemists and largely in this country. Another convention, advocated by Lewis [*J. Am. Chem. Soc.*, **35**, 1 (1913)], is extensively employed in this country. According to this, the potential difference of a metal-solution junction is considered as *positive* when there is a *tendency* for positive electricity to flow from left to right through the junction as *written*, and as *negative* when there is a *tendency* for positive electricity to flow from right to left. A convention based on free energy changes at the electrodes has recently been presented by Hoyt [*J. Chem. Education*, **17**, 530 (1940)]. This is independent of the direction of current flow and applies uniformly in all cases.

**The Mechanism of the Action of Voltaic Cells.** A picture of the mechanism of the action of voltaic cells may be obtained by applying Nernst's theory to the Daniell cell which is shown diagrammatically in Fig. 63. Since the electrolytic solution pressure of the zinc is very much higher than the osmotic pressure of the zinc ions, zinc ions pass from the

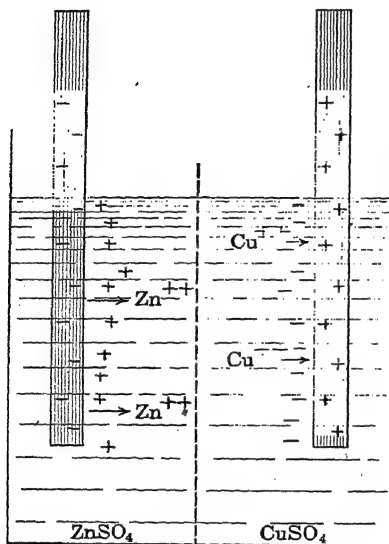


FIG. 63.

metal into the solution leaving the metal negatively charged. In this way an electric double layer and a negative potential difference are established between the metal and the solution. For similar reasons a positive potential difference is established between the copper electrode and the solution of copper sulphate. At both electrodes equilibrium is very quickly established: on the one hand, when the electrolytic solution pressure of the zinc (the force driving zinc ions into the solution) is just balanced by the electrostatic field set up between the metal and the solution, and by the osmotic pressure of the zinc ions in solution; on the other, when the osmotic pressure of the copper ions (the force tending to deposit copper ions on the electrode) is just balanced by the electrostatic

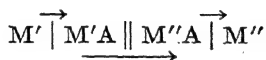
field set up between the solution and the copper electrode, and by the electrolytic solution pressure of the electrode. If now, these equilibria which exist at the electrodes could be removed, more copper would deposit from solution and more zinc would pass from the electrode of that metal into solution in the form of ions. This removal may be accomplished by connecting the electrodes by a wire, which permits the opposite kinds of electricity to neutralize each other. If this is done, zinc ions will continue to pass into, and copper ions out of, solution, and a current will flow through the wire.<sup>1</sup>

**Calculation of the Potential Difference at a Metal-Solution Junction.** Since in the deduction of equation 12 no assumptions were made regard-

<sup>1</sup> It should be emphasized that this picture of the mechanism of current production in a voltaic cell is based upon the hypothetical electrolytic solution pressure of metals. The Nernst theory of electromotive force, involving the concept of electrolytic solution pressure, has been considered kinetically by Butler [*Trans. Faraday Soc.*, 19, 729 (1924)], who has shown it to be justifiable.

ing the mechanism by which the electromotive force of a cell is established, this equation is entirely independent of any theory of the origin of electromotive force. We may, however, acquire a knowledge of the electromotive force of a voltaic cell and a deeper insight into its nature by calculating, according to Nernst, the potential differences which exist between the electrodes and the solutions with which they are in contact.

In order to make this calculation, let us consider the cell



which is maintained at a constant temperature  $T$ , and in which the volumes of the solutions, containing  $n'$  moles of  $\text{M}'\text{A}$  and  $n''$  moles of  $\text{M}''\text{A}$ , are so large that the introduction, or the withdrawal, of 1 gram ion of the metal does not change their osmotic pressures appreciably. Further, let  $P'$  and  $P''$  represent the electrolytic solution pressures of  $\text{M}'$  and  $\text{M}''$ , respectively;  $P'$  and  $P''$  the osmotic pressures of the  $\text{M}'$  and  $\text{M}''$  ions; and  $\pi'$  the potential difference at the junction  $\text{M}' \mid \text{M}'\text{A}$  and  $\pi''$  the potential difference at the junction  $\text{M}''\text{A} \mid \text{M}''$ .

First allow the cell to produce that quantity of electricity which is associated with the passage of 1 gram ion of  $\text{M}'$  from the metal to the solution  $\text{M}'\text{A}$ . Since the solution is known to be positively charged compared to the electrode, the electric force *opposes* the motion of the positive charge. Accordingly, the electrical work involved is

$$A_1 = -z'F\pi'$$

where  $z'$  is the valence of the metal  $\text{M}'$ . Next remove, reversibly, solvent from the solution containing  $\text{M}'\text{A}$ , until its osmotic pressure becomes equal to the electrolytic solution pressure,  $P'$ , of the metal  $\text{M}'$ , whereupon the potential difference at the junction  $\text{M}' \mid \text{M}'\text{A}$  changes to zero. The work expended in this removal of the solvent from the solution is

$$A_2 = - \int_{P'}^{P'} V dP' = -(2n' + 1)RT \ln \frac{P'}{P'}$$

if the laws for ideal solutions are assumed to hold. Now transfer 1 gram ion of the metal  $\text{M}'$  from the solution to the electrode. Since the potential difference between the electrode and the solution is zero, no work will be involved in this operation. Finally, dilute the solution, reversibly, until its osmotic pressure is brought back to  $P'$ , thereby obtaining a quantity of work

$$A_3 = 2n'RT \ln \frac{P'}{P'}$$

Since the total work involved in an isothermal, reversible, cyclic process is zero, it follows that

$$A_1 + A_2 + A_3 = -z'F\pi' - (2n' + 1)RT \ln \frac{P'}{P'} + 2n'RT \ln \frac{P'}{P'} = 0$$

whence

$$-z'F\pi' - RT \ln \frac{P'}{P'} = 0$$

and

$$\pi' = \frac{RT}{z'F} \ln \frac{P'}{P'} \quad (13)$$

Changing from natural logarithms ("ln") to common logarithms ("log"),

$$\pi' = \frac{2.3026RT}{z'F} \log \frac{P'}{P'} \quad (13a)$$

Equation 13 is known as Nernst's equation.

The ratio  $2.3026RT/F$  has the following values, when the gas constant,  $R$ , is expressed in electrical units (8.316):

Absolute temperature =	273°	273 + 18°	273 + 25°	273 + 30°
$2.3026RT/F$	= 0.0541	0.0577	0.0591	0.0601

At room temperature the value of the ratio may be taken as 0.058. On substituting this value in equation 13a, we obtain

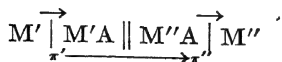
$$\pi' = \frac{0.058}{z'} \log \frac{P'}{P'} \quad (14)$$

From the form of equation 14, it can be seen that a tenfold increase or decrease in the value of the osmotic pressure,  $P'$ , is attended by an *algebraic* increase or decrease in  $\pi'$  of  $0.058/z'$  volts.

For electrodes which are reversible with respect to *negative* ions, the potential is given by the expression

$$\pi = \frac{0.058}{z} \log \frac{P}{P'} \quad (14a)$$

**Calculation of the Electromotive Force of a Voltaic Cell.** In a cell of the type



there are four places at which potential differences may exist:

- 1 and 2. At the metal-solution junctions.
3. At the solution-solution junction.
4. At the metal-metal junction.

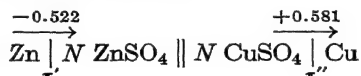
Since the potential difference at the solution-solution junction in cells of this type is very small in comparison with the electrode potentials, we shall neglect it. The potential difference at the metal-metal junction we shall represent by II. As the electromotive force of a voltaic cell is the *algebraic* difference of all the potential differences, it follows that

$$\begin{aligned} E &= \pi'' - \pi' + \text{II} \\ &= \frac{0.058}{z''} \log \frac{P''}{P''} - \frac{0.058}{z'} \log \frac{P'}{P'} + \text{II} \end{aligned} \quad (15)$$

If  $z' = z'' = z$ , then

$$E = \frac{0.058}{z} \left( \log \frac{P''}{P''} - \log \frac{P'}{P'} \right) + \text{II} \quad (15a)$$

In order to avoid errors in obtaining the algebraic difference of the potential differences in a voltaic cell, a good method is to consider the tendency of positive electricity to flow round the circuit, taking the junctions in order. Hence, the correct value is obtained by subtracting the *less* positive potential difference from the *more* positive potential difference. Thus, in the Daniell cell,



the electromotive force is

$$E = +0.581 - (-0.522) = 1.103 \text{ volts}$$

**The Volta Effect.** In 1797, Volta showed that a potential difference exists between two metals in contact. This potential difference, known as the **Volta effect**, has been discussed by Langmuir,<sup>1</sup> Smits and Bijvoet,<sup>2</sup> and Rice.<sup>3</sup> Although for many years electrochemists have believed the contact potentials between metals to be inappreciable, modern investigation in physics has demonstrated that this is not always so.<sup>4</sup> Since it

<sup>1</sup> *Trans. Am. Electrochem. Soc.*, **29**, 125 (1916).

<sup>2</sup> *Proc. Akad. Sci. Amsterdam*, **21**, 562 (1919).

<sup>3</sup> *Science Progress*, **1922**, 362.

<sup>4</sup> Cf. Klein and Lange, *Z. Elektrochem.*, **43**, 570 (1937). In this paper an indirect method for the determination of the Volta potential is described and numerous values are calculated.

is probable, however, that the Volta effect between metals which are in a state of internal equilibrium is really very small, and since, moreover, the magnitude of this effect is unknown, we shall neglect it and write equation 15 simply

$$E = \frac{0.058}{z''} \log \frac{P''}{P'} - \frac{0.058}{z'} \log \frac{P'}{P} \quad (16)$$

Consequently, for the Daniell cell we may write:  $E = 1.103$  volts.

It should be mentioned here that expressions for the electromotive force of reversible voltaic cells, in which the Volta effect does not appear, have been deduced by Smits and Bijvoet.<sup>1</sup>

**The Influence of Concentration on the Electromotive Force of Voltaic Cells.** Since the osmotic pressure of the ions of a solute is proportional to their "effective concentration,"  $C$ , the potential difference at a metal-solution junction must vary with the concentration of the dissolved salt. The effective ion concentration may be determined by a method based upon electromotive force measurements, to be discussed in Chapter XIV. In *dilute* solutions, however,  $C = \alpha c$ , where  $\alpha$  is the conductance ratio or the apparent degree of dissociation and  $c$  is the total concentration of the electrolyte.

If  $\pi'_1$  represents the potential difference at the junction  $M' \mid \overrightarrow{M'A}$  when the concentration of  $M'A$  is  $c'_1$ , then

$$\pi'_1 = \frac{0.058}{z'} \log \frac{P'_1}{P'} = \frac{0.058}{z'} \log \frac{kC'_1}{P'} \quad (17)$$

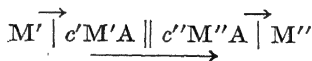
where  $C'_1$  is the effective concentration of the  $M'$  ions. For another concentration,  $c'_2$ , of  $M'A$ , the potential difference at the metal-solution junction is

$$\pi'_2 = \frac{0.058}{z'} \log \frac{P'_2}{P'} = \frac{0.058}{z'} \log \frac{kC'_2}{P'} \quad (18)$$

On subtracting equation 17 from equation 18, we obtain:

$$\pi'_2 = \pi'_1 + \frac{0.058}{z'} \log \frac{C'_2}{C'_1} \quad (19)$$

Accordingly, the influence of concentration on the electromotive force of a voltaic cell of the type



<sup>1</sup> These expressions and their derivation may be found in Smits and Bijvoet's paper (*loc. cit.*) and in Smits' book, *The Theory of Allotropy*, translated by Thomas, pp. 123-125, 1922.

is expressed by the equation

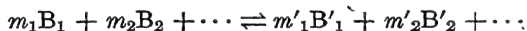
$$E_2 = \pi''_2 - \pi'_2 = E_1 + \frac{0.058}{z''} \log \frac{C''_2}{C''_1} - \frac{0.058}{z'} \log \frac{C'_2}{C'_1} \quad (20)$$

When  $z' = z'' = z$ , and  $C'_1 = C''_1$

$$E_2 = E_1 + \frac{0.058}{z} \log \frac{C''_2}{C'_2} \quad (20a)$$

It is evident from the form of equation 20 or 20a that the electromotive force of a voltaic cell is increased by decreasing the concentration of the solution into which ions are entering, and that it is decreased by diminishing the concentration of the solution from which ions are leaving. Accordingly, the electromotive force of the Daniell cell can be lowered by the addition of potassium cyanide to the solution of copper sulphate, since this removes  $\text{Cu}^{++}$  ions by the formation of complex  $\text{Cu}(\text{CN})_3^{--}$  ions. By progressively decreasing the concentration of the copper ions, the osmotic pressure may be reduced to such an extent that copper ions pass from the metal to the solution, the electromotive force of the cell becomes zero and then changes sign, and the direction of the current through the cell is reversed.

**Electromotive Force and Chemical Equilibrium.** The maximum work (A) that may be obtained from a reversible chemical reaction



is given by the well-known reaction isotherm<sup>1</sup>

$$A = RT \ln K - RT \ln \frac{[\text{B}'_1]^{m'_1} [\text{B}'_2]^{m'_2}}{[\text{B}_1]^{m_1} [\text{B}_2]^{m_2}} \quad (21)$$

In this expression  $K$  is the equilibrium constant of the reaction, and the *bracketed* quantities represent the concentrations of the molecular species taking part in the reaction.<sup>2</sup> The equilibrium constant  $K$  is given by the relation

$$K = \frac{[\text{B}'_{1e}]^{m'_1} [\text{B}'_{2e}]^{m'_2}}{[\text{B}_{1e}]^{m_1} [\text{B}_{2e}]^{m_2}} \quad (22)$$

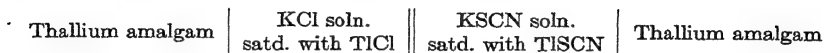
where the subscript  $e$  denotes the *equilibrium* concentration of the reacting substances.

<sup>1</sup> The derivation of this expression will be found in any textbook on theoretical chemistry.

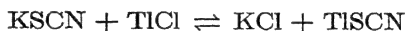
<sup>2</sup> Square brackets will be employed throughout the book to represent the concentrations of the molecular species enclosed within them.



Since the production of electrical energy in a reversible voltaic cell results from a reversible chemical reaction, the electrical energy developed by the cell must be equal to the maximum work that can be done by the reaction. Although the relation between electromotive force and chemical equilibrium was recognized by van't Hoff as early as 1886, it was not until Knüpfner<sup>1</sup> studied the cell



that the relation was tested experimentally. The reaction which takes place in this cell is given by the equation



Since solid TlCl and TlSCN are present in the cell, the concentrations of these substances remain constant. Therefore, in applying the reaction isotherm (equation 21), the saturated, constant concentrations may be included in the equilibrium constant, and we may write:

$$A = FE = RT \ln K - RT \ln \frac{[\text{KCl}]}{[\text{KSCN}]}$$

or

$$E = \frac{RT}{F} \ln K - \frac{RT}{F} \ln \frac{[\text{KCl}]}{[\text{KSCN}]} \quad (23)$$

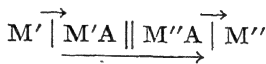
The agreement between the value of  $E$  obtained by means of equation 23 and that found by direct measurement is shown by Knüpfner's data in Table LI.

TABLE LI

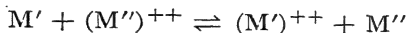
EXPERIMENTAL VERIFICATION OF THE RELATION BETWEEN ELECTROMOTIVE FORCE AND CHEMICAL EQUILIBRIUM

$T$	$K$	$\frac{[\text{KCl}]}{[\text{KSCN}]}$	$E$ (Calculated) volts	$E$ (Observed) volts
273 + 0.8	1.74	1.55	+0.0027	+0.0037
273 + 20.0	1.24	1.52	-0.0052	-0.0048
273 + 39.9	0.85	1.50	-0.0153	-0.0141

Let us now consider the cell



in which the reaction



<sup>1</sup> *Z. physik. Chem.*, **26**, 255 (1898).

takes place. The electromotive force of this cell is given by the expression

$$E = \frac{RT}{2F} \ln K - \frac{RT}{2F} \ln \frac{[(M')^{++}]}{[(M'')^{++}]} \quad (24)$$

When the concentrations of the two ions are equal,

$$E = E_1 = \frac{RT}{2F} \ln K \quad (25)$$

Therefore, for any concentrations of  $(M')^{++}$  and  $(M'')^{++}$ , at room temperature,

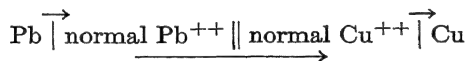
$$E = E_1 + \frac{0.058}{2} \log \frac{C''}{C'} \quad (26)$$

where  $C'$  and  $C''$  are the effective concentrations of the ions  $(M')^{++}$  and  $(M'')^{++}$ , respectively. This equation, the derivation of which involves no other assumption than the laws of thermodynamics and solutions, is identical with equation 20a, which was deduced on the assumption of a hypothetical electrolytic solution pressure.

The equilibrium constants of reactions which take place in most reversible voltaic cells are too large to be determined experimentally, owing to the fact that the reactions proceed to so-called completion. These constants may, however, be calculated from electromotive force measurements by means of equation 25. For example, let us calculate the equilibrium constant of the reaction



Since the electromotive force of the cell



is 0.472 volt at 25°, it follows that

$$E_1 = 0.472 = \frac{RT}{2F} \ln K$$

Therefore,

$$\log K = \frac{2 \times 0.472}{0.0591} = 16 \text{ (approx.)}$$

and

$$K = \frac{[\text{Pb}_e^{++}]}{[\text{Cu}_e^{++}]} = 10^{16}$$

Accordingly, in the above cell, lead ions will enter solution and copper ions leave solution, until the concentration of the lead ions is  $10^{16}$  times as great as that of the copper ions.

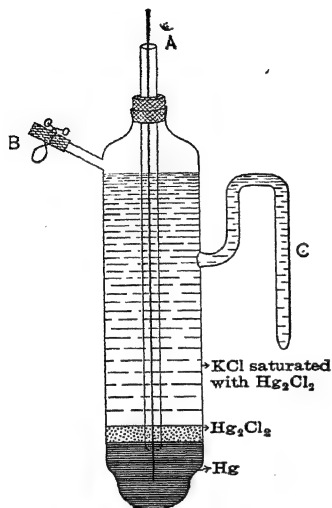
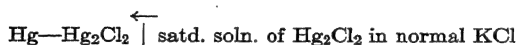


FIG. 64.

**Standard Electrodes.** In order to measure the potential difference at a metal-solution junction, it is necessary to have another metal-solution junction, or "half-element," of known potential difference. Such metal-solution junctions are termed **standard electrodes**. The **normal calomel electrode** and the **deci-normal calomel electrode** are standards which are very frequently employed in the measurement of electrode potentials. These electrodes (Fig. 64) consist of mercury and a paste of mercurous chloride in contact with a normal, or a deci-normal, solution of potassium chloride that is saturated with mercurous chloride. Electrical connection is made with the mercury by means of a piece of wire sealed in the glass tube A. In using the electrode, the tube, C, is filled with a

normal, or a deci-normal, solution of potassium chloride by applying suction at B.

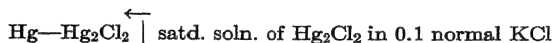
The potential of the normal calomel, or Ostwald, electrode,



at any temperature,  $t$ , is given by the expression:

$$\pi = 0.5606 + 0.0006(t - 18) \text{ volt} \quad (27)$$

The potential of the deci-normal calomel electrode



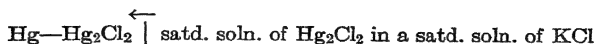
is

$$\pi = 0.618 + 0.0008(t - 18) \text{ volt} \quad (28)$$

The use of a saturated potassium chloride-calomel electrode, in place of the normal or the deci-normal calomel electrode, has been proposed.<sup>1</sup>

<sup>1</sup> Fales and Mudge, *J. Am. Chem. Soc.*, **42**, 2434 (1920).

The potential of this electrode



between 5° and 60° is given by the expression

$$\pi = 0.5266 + 0.00020(t - 25) \text{ volt.} \quad (29)$$

The potentials of these and several other standard electrodes at 25° are given in Table LII.

TABLE LII

STANDARD ELECTRODE POTENTIALS AT 25°<sup>1</sup>

Electrode	Potential
$\text{Hg} - \text{Hg}_2\text{Cl}_2 \mid N \text{ KCl}$	+0.5648 volt
$\text{Hg} - \text{Hg}_2\text{Cl}_2 \mid 0.1 N \text{ KCl}$	+0.624 volt
$\text{Hg} - \text{Hg}_2\text{Cl}_2 \mid \text{satsd. KCl}$	+0.5266 volt
$\text{Hg} - \text{Hg}_2\text{SO}_4 \mid N \text{ SO}_4^{--}$	+0.9039 volt
$\text{Hg} - \text{HgO} \mid N \text{ OH}^-$	+0.3810 volt
$\text{Ag} - \text{AgCl} \mid N \text{ Cl}^-$	+0.5071 volt

The above-mentioned standard electrodes, which are reversible with respect to *negative* ions, are called **electrodes of the second class**. Electrodes which are reversible with respect to *positive* ions are called **electrodes of the first class**. The potentials of a number of electrodes of the first class, at 18°, are given in Table LIII.

TABLE LIII

SINGLE ELECTRODE POTENTIALS AT 18°

Electrode	Potential
$\text{Mg} \mid 1.0 N \text{ MgSO}_4$	-1.45 volts
$\text{Mn} \mid 1.0 N \text{ MnSO}_4$	-0.815 volt
$\text{Zn} \mid 1.0 N \text{ ZnSO}_4$	-0.522 volt
$\text{Cd} \mid 1.0 N \text{ CdSO}_4$	-0.152 volt
$\text{Ni} \mid 1.0 N \text{ NiSO}_4$	+0.01 volt
$\text{Pb} \mid 1.0 N \text{ Pb(NO}_3)_2$	+0.126 volt
$\text{Cu} \mid 1.0 N \text{ CuSO}_4$	+0.581 volt
$\text{Ag} \mid 0.5 N \text{ AgNO}_3$	+1.049 volts

**The Measurement of Single Electrode Potentials.** In order to determine the potential difference of any metal-solution junction, the

<sup>1</sup> It must be borne in mind that there is much uncertainty as to the *absolute* values of electrode potentials.

metal is immersed in the solution which is contained in a vessel like that shown in Fig. 64. The metal-solution junction is then combined with a standard electrode to form a voltaic cell, by means of an intermediate solution of potassium chloride (normal), as indicated in Fig. 65. The electromotive force of the cell is determined as previously described.

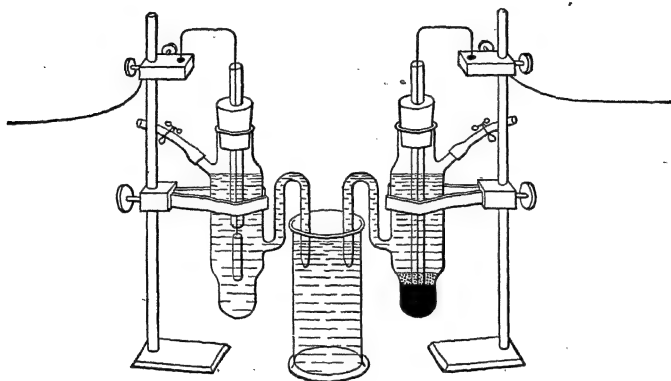
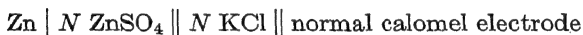


FIG. 65.

Since the potential difference of the standard electrode is known, that of the metal-solution junction may be calculated. Thus, since the electromotive force of the combination



is 1.082 volts at 18° the single potential of the  $\text{Zn} \mid N \text{ZnSO}_4$  junction must be  $-0.522$  volt.

When the solution of the second electrode is alkaline, it should be combined with an alkaline standard electrode; when acid, with an acid standard electrode.

The potential difference at one of the electrodes of an electrolytic cell or tank may be determined as follows: The side arm of a standard electrode is lengthened and drawn out to a capillary, the end of which is pressed against the electrode of the electrolytic vessel. The electromotive force of the cell so formed is measured in the usual way, and the potential difference of the electrode in question is calculated from the value obtained.<sup>1</sup>

<sup>1</sup> Haber, *Z. physik. Chem.*, **32**, 207 (1900); Foerster and Müller, *Z. Elektrochem.*, **9**, 200 (1903).

**Null Electrodes.** The potential difference of a standard electrode is determined by combining it with another metal-solution junction having a zero potential difference. Such an electrode is called a **null electrode**. The potential difference between mercury and a solution of a double cyanide is zero. A null electrode may be formed also by progressively adding potassium cyanide to a solution of copper sulphate in contact with copper, until the positive charge on the metal is reduced to zero. The **dropping electrode** is still another form of null electrode.<sup>1</sup> In this electrode, a stream of drops of mercury is allowed to fall through a normal solution of potassium chloride, containing a small concentration of mercurous chloride, from an orifice dipping just below the surface of the solution (see Fig. 62). From our discussion of Palmer's experiment (p. 178), it is evident that mercurous ions will continue to be removed from the upper layers of the solution, until the osmotic pressure of these ions is equal to the electrolytic solution pressure of mercury, i.e., until the potential difference between the mercury and the solution is reduced to zero. This condition is approximately reached fairly quickly; but it can never be completely attained, on account of diffusion of mercurous ions from the lower to the upper layers of the solution.

When a drop of mercury is placed in a tube containing a solution of an electrolyte, in which there is a fall of potential, the drop moves towards the positive or negative electrode, depending on the concentration of the mercurous ions contained in the solution. This behavior was used by Bodforss<sup>2</sup> to determine the absolute null point of electric potential. The results of his experiments gave for the absolute potential of the normal calomel electrode a value very much lower than those previously obtained. After a critical review of the methods employed in the past, Billiter<sup>3</sup> concluded that the only trustworthy one is that of Bennewitz and Schulz,<sup>4</sup> in which a fresh metal surface is produced continuously. However, from a consideration of his own work and that of Farkas,<sup>5</sup> Baur<sup>6</sup> found no reason to depart from the accepted value for the absolute potential of the normal calomel electrode. From a study of the variation of potential difference with interfacial tension of mercury, a mean value of  $0.563 \pm 0.004$  volt was obtained<sup>7</sup> for the absolute poten-

<sup>1</sup> Cf. Paschen, *Wied. Ann.*, **41**, 42 (1890); Craxford, *Phil. Mag.*, **16**, 66, 268 (1933).

<sup>2</sup> *Z. Elektrochem.*, **29**, 121 (1923).

<sup>3</sup> *Trans. Electrochem. Soc.*, **57**, 351 (1930).

<sup>4</sup> *Z. physik. Chem.*, **124**, 115 (1926); cf. Bennewitz and Bigalke, *ibid.*, A154, 113 (1931).

<sup>5</sup> *Z. Elektrochem.*, **38**, 654 (1932).

<sup>6</sup> *Ibid.*, **38**, 665 (1932).

<sup>7</sup> Hirota and Murata, *Bull. Chem. Soc. Japan*, **10**, 594 (1935).

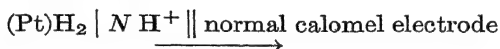
tial of the normal calomel electrode; and a value of 0.50 volt was calculated from the free energies of dissolution of the individual ions.<sup>1</sup>

**Reference Electrodes.** Few problems in electrochemistry continue to give rise to so much disagreement as the absolute values of single electrode potentials. On account of the uncertainty of these values, it is customary to refer them to the potential of the standard electrode *taken as zero*. Indeed, this is the way in which the normal calomel electrode is most frequently employed. Thus, while the absolute potential of the electrode,  $\text{Zn} \mid \text{N ZnSO}_4$ , is  $\pi_a = -0.522$  volt, when referred to the normal calomel electrode as zero it is  $\pi_c = -1.082$  volts. If, therefore, we represent the potential of an electrode by  $\pi_c$ , when referred to the normal calomel electrode as zero, then  $\pi_c$  is equal to the electromotive force ( $E$ ) of the cell,<sup>2</sup> electrode-normal calomel electrode. Hence, the absolute potential of an electrode (at 25°) is

$$\pi_a = E + 0.5648 = \pi_c + 0.5648 \quad (30)$$

Another important standard zero electrode extensively employed in electromotive force measurements consists of hydrogen, at atmospheric pressure, in contact with a normal solution of hydrogen ions. (This type of electrode, known as a gas electrode, will be discussed in the following chapter.) This electrode, which is called the **normal hydrogen electrode** or the Nernst electrode, has many advantages. It is easily prepared by immersing a piece of well-platinized platinum in a solution of sulphuric acid which is normal with respect to hydrogen ions. Arkadiev<sup>3</sup> found that the potential of an hydrogen electrode is increased by the presence of neutral salts, the increase being proportional to the concentration of the salt.

Since, at 25°, the electromotive force of the cell



is 0.2805 volt, the potential of the normal hydrogen electrode referred to the normal calomel electrode as zero is  $\pi_c = -0.2805$  volt; and the potential of the normal calomel electrode referred to the normal hydrogen electrode as zero is  $\pi_h = +0.2805$  volt. The absolute potential of

<sup>1</sup> Latimer, Pitzer, and Slansky, *J. Chem. Phys.*, **7**, 108 (1939).

<sup>2</sup> If the electrode is more positive than the reference electrode, i.e., if the current actually flows from the solution to the electrode when the cell produces electricity, the sign of  $E$  is *positive*, and *vice versa*.

<sup>3</sup> *Z. physik. Chem.*, **104**, 192 (1923).

the normal hydrogen electrode is, therefore, +0.2843 volt. The absolute potential ( $\pi_a$ ) of an electrode and its potential referred to the normal hydrogen electrode as zero ( $\pi_h$ ), both at 25°, are related as follows:

$$\pi_a = \pi_h + 0.2843 \quad (31)$$

**Electrolytic Potentials.** When the concentration of the ions is molal, the potential of any reversible electrode is called the **electrolytic potential** ( $\pi^\circ$ ) of the electrode, or the **normal electrode potential**. Since a single electrode potential, as we have seen, is given by the expression

$$\pi = \frac{RT}{zF} \ln \frac{kC}{P} \quad (32)$$

it is evident that

$$\pi^\circ = -\frac{RT}{zF} \ln \frac{P}{k} \quad (33)$$

It would appear from this equation that the electrolytic solution pressure of an electrode material is a quantity the logarithm of which is proportional to the electrolytic potential of the electrode.

On subtracting equations 32 and 33, we obtain:

$$\pi^\circ = \pi - \frac{RT}{zF} \ln C \quad (34)$$

By means of this equation the electrolytic potential of an electrode may be calculated from any measured electrode potential.

Since single electrode potentials are usually referred to the normal hydrogen or the normal calomel electrode as zero, it is customary to refer electrolytic potentials to these normal electrodes. Table LIV gives the electrolytic potentials, at 25°, of a number of electrodes, referred to both the normal calomel electrode ( $\pi^\circ_c$ ) and the normal hydrogen electrode ( $\pi^\circ_h$ ) as zero. The relation between the electrolytic potentials expressed on the two scales is

$$\pi^\circ_c = \pi^\circ_h - 0.2805 \quad (35)$$

Regarding the signs of the electrolytic potentials given in the table, a *positive* electrolytic potential means that the electrode is the *positive* pole of a cell formed by combining the electrode with the standard electrode, while a *negative* electrolytic potential means that the electrode is the *negative* pole of such a cell.



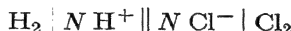
TABLE LIV

## ELECTROLYTIC POTENTIALS AT 25°

Electrode	$\pi_{\text{c}}$	$\pi_{\text{h}}$	Authority
Li, Li <sup>+</sup>	-3.240 <sub>0</sub>	-2.959 <sub>5</sub>	<i>International Critical Tables</i>
Rb, Rb <sup>+</sup>	-3.206 <sub>4</sub>	-2.925 <sub>9</sub>	<i>International Critical Tables</i>
K, K <sup>+</sup>	-3.204 <sub>6</sub>	-2.924 <sub>1</sub>	<i>International Critical Tables</i>
Cs, Cs <sup>+</sup>	-3.204	-2.923	Bent and Forbes <sup>1</sup>
Ca, Ca <sup>++</sup>	-3.04 <sub>3</sub>	-2.76 <sub>3</sub>	<i>International Critical Tables</i>
Na, Na <sup>+</sup>	-2.9937	-2.7132	Smith and Taylor <sup>2</sup>
Mg, Mg <sup>++</sup> (18°)	-2.146	-1.866	Beck <sup>3</sup>
Al, Al <sup>+++</sup>	-1.97	-1.69	Latimer and Greensfelder <sup>4</sup>
Zn, Zn <sup>++</sup>	-1.038	-0.758	Horsch <sup>5</sup>
Ga, Ga <sup>+++</sup>	-0.80	-0.52	Bergkampff <sup>6</sup>
Fe, Fe <sup>++</sup>	-0.7207	-0.4402	Randall and Frandsen <sup>7</sup>
Cd, Cd <sup>++</sup>	-0.675	-0.395	Getman <sup>8</sup>
Tl, Tl <sup>+</sup>	-0.6192	-0.3387	Richards and Smyth <sup>9</sup>
Co, Co <sup>++</sup>	-0.549	-0.268	Heymann and Jelinek <sup>10</sup>
Ni, Ni <sup>++</sup>	-0.511	-0.231	Haring and Bosche <sup>11</sup>
Sn, Sn <sup>++</sup>	-0.4211	-0.1406	Haring and White <sup>12</sup>
Pb, Pb <sup>++</sup>	-0.4056	-0.1251	Haring and Zapponi <sup>13</sup>
H <sub>2</sub> , H <sup>+</sup>	-0.2805	0.0000	
Cu, Cu <sup>++</sup>	-0.063 <sub>6</sub>	+0.344 <sub>1</sub>	<i>International Critical Tables</i>
S, S <sup>-</sup>	+0.20	+0.48	Watanabe <sup>14</sup>
Te, Te <sup>++++</sup>	+0.2877	+0.5682	Getman <sup>15</sup>
I <sub>2</sub> , I <sup>-</sup>	+0.2540	+0.5345	Jones and Kaplan <sup>16</sup>
Hg, Hg <sub>2</sub> <sup>++</sup>	+0.5185	+0.7986	<i>International Critical Tables</i>
Ag, Ag <sup>+</sup>	+0.5195	+0.7996	Lingane and Larson <sup>17</sup>
Br <sub>2</sub> , Br <sup>-</sup>	+0.784 <sub>3</sub>	+1.064 <sub>3</sub>	<i>International Critical Tables</i>
Cl <sub>2</sub> , Cl <sup>-</sup>	+1.0778	+1.3583	<i>International Critical Tables</i>
Au, Au <sup>+++</sup>	+1.08	+1.36	Jirsa and Jelinek <sup>18</sup>
F <sub>2</sub> , F <sup>-</sup>	+2.57	+2.85	Latimer <sup>19</sup>

<sup>1</sup> *J. Am. Chem. Soc.*, **61**, 709 (1939).<sup>2</sup> *J. Research Natl. Bur. Standards*, **25**, 731 (1940).<sup>3</sup> *Rec. trav. chim.*, **41**, 353 (1922).<sup>4</sup> *J. Am. Chem. Soc.*, **50**, 2202 (1928).<sup>5</sup> *Ibid.*, **41**, 1787 (1919).<sup>6</sup> *Z. Elektrochem.*, **38**, 847 (1932).<sup>7</sup> *J. Am. Chem. Soc.*, **54**, 47 (1932).<sup>8</sup> *J. Phys. Chem.*, **35**, 588 (1931).<sup>9</sup> *J. Am. Chem. Soc.*, **44**, 524 (1922).<sup>10</sup> *Z. physik. Chem.*, **A160**, 34 (1932).<sup>11</sup> *J. Phys. Chem.*, **33**, 161 (1929).<sup>12</sup> *Trans. Electrochem. Soc.*, **73**, 211 (1938).<sup>13</sup> *Ibid.*, **75**, 473 (1939).<sup>14</sup> *Sci. Reports Tohoku Imp. Univ.*, **22**, 414 (1933).<sup>15</sup> *Trans. Electrochem. Soc.*, **64**, 201 (1933).<sup>16</sup> *J. Am. Chem. Soc.*, **50**, 2066 (1928).<sup>17</sup> *Ibid.*, **58**, 2647 (1936).<sup>18</sup> *Chem. Listy*, **18**, 1 (1929).<sup>19</sup> *J. Am. Chem. Soc.*, **48**, 2868 (1926).

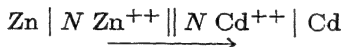
The electromotive force of a cell formed by combining two normal electrodes is equal to the algebraic difference of their electrolytic potentials. Thus, at 25°, the electromotive force of the cell



is

$$E = \pi^\circ_{\text{Cl}} - \pi^\circ_{\text{H}} = 1.078 - (-0.2805) = 1.359 \text{ volts}$$

and that of the cell



is

$$E = \pi^\circ_{\text{Cd}} - \pi^\circ_{\text{Zn}} = -0.395 - (-0.758) = 0.363 \text{ volt}$$

The order in which the elements are arranged in Table LIV is the order of the familiar **electromotive series**. All metals with an electrolytic potential less than that of hydrogen displace hydrogen ions from solution.

In determining the values given in Table LIV the Volta effect has been assumed to be negligible. According to Smits,<sup>1</sup> however, "so long as the *Volta effect* is unknown, it is impossible to draw any conclusions from the so-called electromotive series with regard to the order followed by the metallic ions..." He points out that while it is generally assumed that

$$\pi^\circ_{\text{M}'} \text{ is more positive than } \pi^\circ_{\text{M}''}$$

if a metal M' is more positive than a metal M'' in normal solutions of their ions, this assumption is incorrect. Measurement merely shows that

$$\pi^\circ_{\text{M}''} + \text{II is more positive than } \pi^\circ_{\text{M}'} + \text{II}$$

where, as previously, II stands for the Volta effect.

Scarpa<sup>2</sup> has corrected the electrolytic potentials of the metals for the Volta effect.

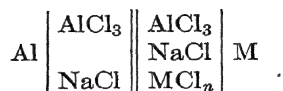
The determination of the electrode potentials of lithium, sodium, potassium, rubidium, calcium, zinc, cadmium, lead, hydrogen, copper, and silver in anhydrous hydrazine shows that these elements fall into three classes: (1) the alkali metals and calcium, having potentials almost the same as those in water; (2) zinc, cadmium, and lead, for which the potentials in hydrazine are 0.5 to 0.8 volt more negative compared with those in water; (3) hydrogen, copper, and silver, for which a similar but larger (up to 1.22 volts) displacement is observed.<sup>3</sup>

<sup>1</sup> *The Theory of Allotropy*, p. 123, 1922.

<sup>2</sup> *Atti accad. Lincei*, [vi], **29**, 441 (1939).

<sup>3</sup> Pleskov, *Acta Physicochim. U.R.S.S.*, **13**, 662 (1940).

**Electrode Potentials in Fused Salts.** Determinations of the electromotive force of cells of the type



where M is copper, iron, zinc, or manganese, have been made at 400°, 500°, and 600°, the AlCl<sub>3</sub> and NaCl being present in equimolecular proportions.<sup>1</sup> The values obtained were found to increase with temperature and, with the exception of manganese chloride, with the concentration of the MCl<sub>n</sub>. All the metals were more noble than aluminum. For the ratio MCl<sub>n</sub> : AlCl<sub>3</sub> = 1 : 10, the electrode potentials given in Table LV were obtained.

TABLE LV  
ELECTRODE POTENTIALS IN FUSED SALTS

Electrode	Temperature	$\pi$ in volts
Mn, Mn <sup>++</sup>	500°	0.12
Zn, Zn <sup>++</sup>	365	0.36
Cu, Cu <sup>+</sup>	500	0.81
Cu, Cu <sup>++</sup>	500	0.84
Fe, Fe <sup>+++</sup>	500	> 1

**Heat of Ionization.** It was shown experimentally by Jahn<sup>2</sup> that the Gibbs-Helmholtz equation (11 and 12) is applicable to single electrode potentials, as well as to the electromotive force of the whole cell. Hence

$$\pi = \frac{-q}{zF} + T \frac{d\pi}{dT} \quad (36)$$

where  $-q$  is the heat of ionization of the electrode material, i.e., the heat evolved when 1 gram ion is formed at the electrode, and  $\pi$  is the electrode potential. On solving equation 36 for  $q$ , we obtain

$$q = - \left( \pi - T \frac{d\pi}{dT} \right) zF \quad (37)$$

By means of this equation,  $q$  may be calculated, provided that the electrode potential and its temperature coefficient are known; *vice versa*,  $\pi$

<sup>1</sup> Plotnikov, Kirichenko, and Fortunatov, *Zapiski Inst. Khim. Ukr. Akad. Nauk U.S.S.R.*, 7, 159 (1940).

<sup>2</sup> *Z. physik. Chem.*, 18, 399 (1894).

may be calculated when the other factors are known. For example, Jones and Schumb<sup>1</sup> found for the electrode  $\text{Tl} \mid \text{N Tl}^+$  that  $\pi = -0.0576$  volt at  $25^\circ$  and  $d\pi/dT = -0.00121$ . On substituting these values in equation 37, we get

$$q = -[-0.0576 - 298(-0.00121)] \frac{96,500}{4.182}$$

$$= 6990 \text{ calories}$$

for the heat of the reaction  $\text{Tl} = \text{Tl}^+ + \ominus$ .

**The Influence of Negative Ions on the Metal-Solution Potential Difference.** In order to determine whether the negative ions exert an influence upon the potential difference at the point of contact of a metal with its own ions, Neumann<sup>2</sup> measured the potential difference between thallium and 0.01 normal solutions of more than twenty thallium salts. As in these solutions the degrees of dissociation of the salts are approximately equal, the same potential differences might be expected, provided that the negative ions were without influence. Since Neumann found that the measured values did not differ from each other by more than 1 millivolt, it may be assumed that the negative ion exerts no influence on the potential difference at the point of contact of a metal with its ions. Nevertheless, certain exceptions to this generalization are known.

#### REFERENCE

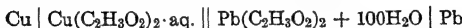
GERKE, "Summary of Electrode Potentials," *Chem. Revs.*, **1**, 377-395 (1925)

#### PROBLEMS

1. A Weston cell and a cell of unknown electromotive force are placed in the same circuit with a galvanometer. When the cells are arranged in series the deflection of the galvanometer is 129 divisions; when they are opposed to one another, the deflection of the galvanometer is 5 divisions. Calculate the electromotive force of the unknown cell.

2. In determining the electromotive force of a voltaic cell by the Poggendorff compensation method, it was found that the point of balance on the bridge wire with a Weston cell and with the unknown cell was 40 and 27.9, respectively. Calculate the electromotive force of the unknown cell.

3. Calculate the electromotive force at  $0^\circ$  of the cell



being given that  $q = -17,533$  calories at  $0^\circ$ , and that  $dE/dT = +0.000385$  volt.

<sup>1</sup> *Proc. Am. Acad. Arts Sci.*, **56**, 199 (1921).

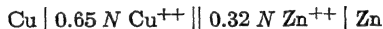
<sup>2</sup> *Z. physik. Chem.*, **14**, 193 (1894).

4. The electromotive force of the cell

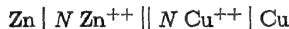


is 1.0962 volts at 0° and 1.0963 volts at 3°. What is the heat of the reaction which takes place in the cell?

5. Calculate the electromotive force of the cell



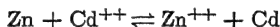
6. The electromotive force of the cell



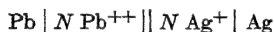
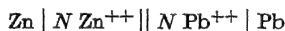
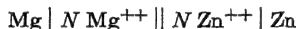
is 1.098 volts at 18°. What is the electromotive force of the cell, when the concentration of the zinc ion is 0.4 and that of the copper ion is 0.0001 gram ion per liter?

7. The potential difference at the junction  $\text{Cu} \mid \text{molal Cu}^{++}$  is +0.620 volt at 25°. Calculate the value to which the concentration of the copper ions would have to be reduced so that the potential difference at this junction would be zero.

8. At 25° the potential difference of the electrode  $\text{Zn} \mid N \text{ Zn}^{++}$  is -0.48 volt, and that of the electrode  $\text{Cd} \mid N \text{ Cd}^{++}$  is -0.12 volt. Calculate the value of the equilibrium constant of the reaction

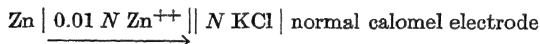


9. What is the electromotive force and the direction of the current of the following combinations:



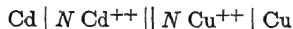
10. Calculate the electromotive force of each of the preceding combinations, when the elements are in contact with solutions which are 0.5 normal with respect to their ions.

11. The electromotive force of the cell



is 1.099 volts at 25°. Calculate the electrolytic potential of zinc, referred to the normal calomel electrode as zero.

12. Write down the reaction which takes place in the cell



and calculate the maximum work of the reaction.

13. If an excess of metallic iron is added to a solution containing  $N \text{ Cu}^{++}$ , calculate the approximate concentration of the copper ions when equilibrium is established.

## CHAPTER IX

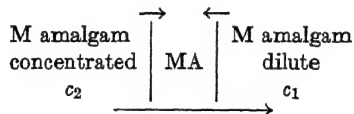
### ELECTROMOTIVE FORCE OF CONCENTRATION CELLS

We shall now consider a type of reversible voltaic cell known as a **concentration cell**. This cell, which is usually much simpler than those we have dealt with, consists essentially of one kind of electrode material and a solution containing ions of this material. Concentration cells are divided into two classes:

(a) Those in which the substance *producing the ions* is of different concentrations.

(b) Those in which the *ions* are of different concentrations.

**Amalgam Cells.** A concentration cell in which the substance producing the ions is of different concentrations is formed when two amalgams, containing different concentrations of the same metal, are placed in a solution of a salt of the metal. In order to determine the relation which exists between the electromotive force of such a cell and the concentrations of the metal in the amalgam electrodes, let us consider the cell



in which  $P_2$  and  $c_2$  represent the electrolytic solution pressure and the concentration, respectively, of the metal in the concentrated amalgam;  $P_1$  and  $c_1$  the corresponding quantities for the dilute amalgam; and  $P$  the osmotic pressure of the solution of the salt, MA. The potential difference at the point of contact of the concentrated amalgam and the solution is, evidently,

$$\pi_2 = \frac{0.058}{z} \log \frac{P}{P_2}$$

and that at the point of contact of the dilute amalgam and the solution is

$$\pi_1 = \frac{0.058}{z} \log \frac{P}{P_1}$$

Accordingly, the electromotive force of the cell is

$$E = \pi_1 - \pi_2 = \frac{0.058}{z} \log \frac{P_2}{P_1}$$

On the assumption that the electrolytic solution pressure of the metal in the concentrated and dilute amalgams is proportional to its respective concentration, we obtain:

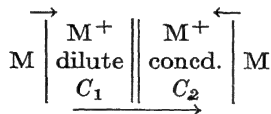
$$E = \frac{0.058}{z} \log \frac{c_2}{c_1} \quad (1)$$

The close agreement between the values of the electromotive force of amalgam cells calculated by means of equation 1 and those determined by experiment is shown by Meyer's results<sup>1</sup> given in Table LVI. The accuracy of equation 1 was also established by Richards and Forbes<sup>2</sup> and by Hildebrand.<sup>3</sup>

TABLE LVI  
ELECTROMOTIVE FORCE OF ZINC AMALGAM CELLS

Temperature	Concentration of:		Electromotive Force $E$	
	Dilute Amalgam $c_1$	Concentrated Amalgam $c_2$	Observed Volt	Calculated Volt
0.0°	0.0000608	0.002280	0.0452	0.0426
58.2°	0.0000608	0.002280	0.0520	0.0517
60.0°	0.0000608	0.002280	0.0520	0.0519
11.6°	0.00011305	0.003366	0.0419	0.0416
18.0°	0.00011305	0.003366	0.0433	0.0425

Cells in Which the Ions are of Different Concentrations (Cells with Transference). As an example of this class, let us take the cell



<sup>1</sup> *Z. physik. Chem.*, **7**, 477 (1891).

<sup>2</sup> *Carnegie Inst. Publ.*, **56** (1906); also *Z. physik. Chem.*, **58**, 683 (1907). Cf. Richards and Conant, *J. Am. Chem. Soc.*, **44**, 601 (1922).

<sup>3</sup> *Trans. Am. Electrochem. Soc.*, **22**, 335 (1913).

Obviously, the electrode potentials must be of the same sign, and the direction of the current determined by the greater potential difference. The source of the electrical energy produced by this type of cell is to be found in the tendency of the concentrations of the two solutions to become equal. When this occurs, the electrode potentials are equal in magnitude and, since they are of the same sign, a current cannot flow through the cell. Cells of this type are extensively employed in electrometric measurements. It is important to know, therefore, the relation between the electromotive force of the cell and the effective concentrations ( $C$ ) of the ions in the dilute and concentrated solutions.

In the above cell, let  $P$  represent the electrolytic solution pressure, and  $z$  the valence, of the metal;  $P_1$  and  $C_1$  the osmotic pressure and the effective concentration of the ions in the dilute solution; and  $P_2$  and  $C_2$  the corresponding quantities for the concentrated solution. Since, in this case,  $P_1 = P_2 = P$  and  $z_1 = z_2 = z$ , equation 16, Chapter VIII, takes the form

$$E = \pi_2 - \pi_1 = \frac{0.058}{z} \log \frac{P_2}{P_1}$$

or, since the osmotic pressures are proportional to the concentrations of the ions,

$$E = \frac{0.058}{z} \log \frac{C_2}{C_1} \quad (2)$$

This equation was first deduced by Nernst.

Electromotive forces calculated by means of equation 2 do not usually agree with values obtained by direct measurement, because the potential difference at the surface of contact of the two solutions is *seldom negligible* in cells of this type. Since these potential differences evade direct measurement, rigorous calculation, or complete elimination, they are a source of perplexity in electromotive force measurements. In order to obtain a more accurate expression for the electromotive force of concentration cells of this type, it is necessary to take the liquid-liquid potential difference into consideration.

**The Potential Difference at the Liquid-Liquid Junction.** The potential difference at the junction of a dilute and a concentrated solution, as explained by Nernst,<sup>1</sup> is due to a migration of ions from the concentrated to the dilute solution. Only when the cation and the anion have the same velocity is the potential difference at the interface zero. If one kind of ion, say, the cation, has a higher velocity than the other, it is evident that the dilute solution will become charged positively and the

<sup>1</sup> *Z. physik. Chem.*, **2**, 613 (1888).



concentrated solution negatively, and that an electric double layer will be formed at the junction of the solutions. The magnitude of this potential difference does not continue to increase as diffusion proceeds, for electrostatic forces come into play and soon equalize the velocities of the two kinds of ions. The potential difference ( $\pi_3$ ) at the liquid-liquid junction of the cell represented above can be calculated as follows:

Let the cell produce  $zF$  coulombs of electricity, by allowing the current to flow through the cell from left to right. During the production of this quantity,  $u/(u+v)$  (the transference number of the cation) gram ion of the metal M is transferred from the dilute to the concentrated solution, whereby the concentration of the ions transferred is increased from  $C_1$  to  $C_2$ . Accordingly, there is expended at the interface a quantity of work

$$A_1 = \frac{u}{u+v} RT \ln \frac{C_2}{C_1}$$

At the same time,  $v/(u+v)$  gram ion of the anion A is carried from the concentrated to the dilute solution, and there is produced a quantity of work

$$A_2 = \frac{v}{u+v} RT \ln \frac{C_2}{C_1}$$

The total work performed at the interface is

$$A = A_2 - A_1 = \frac{v-u}{u+v} RT \ln \frac{C_2}{C_1}$$

Since the electrical work done at the junction of the two solutions during the passage of  $zF$  coulombs is

$$A = zF\pi_3$$

we may write

$$zF\pi_3 = \frac{v-u}{u+v} RT \ln \frac{C_2}{C_1}$$

whence

$$\pi_3 = \frac{v-u}{u+v} \frac{RT}{zF} \ln \frac{C_2}{C_1} \quad (3)$$

or

$$\pi_3 = \frac{v-u}{u+v} \frac{0.058}{z} \log \frac{C_2}{C_1} \quad (3a)$$

This expression shows that, when the transference number of the anion is greater than that of the cation, the potential difference at the junction of the solutions is positive, and *vice versa*.

On combining equations 2 and 3a, we obtain for the electromotive force of the cell

$$E = \pi_2 + \pi_3 - \pi_1 = \frac{2v}{u+v} \frac{0.058}{z} \log \frac{C_2}{C_1} \quad (4)$$

or

$$E = 2n_a \frac{0.058}{z} \log \frac{C_2}{C_1} \quad (4a)$$

where  $n_a$  is the transference number of the anion. It will be observed that  $E$  is larger, the greater the difference between the concentrations of the two solutions. When, for example,  $n_a = 0.5$  and  $z = 1$ , the electromotive force of the cell is 0.058,  $2 \times 0.058$ , and  $3 \times 0.058$  volt for the concentration ratios 10 : 1, 100 : 1, and 1000 : 1.

Equation 4 may be derived directly by calculating the maximum work ( $A$ ) which is produced when 1 gram ion of metal is transferred from the left-hand to the right-hand electrode, at constant temperature. As before, allow the cell to produce  $zF$  coulombs of electricity, whereby 1 gram ion of the metal passes from the left-hand electrode into the dilute solution and the same quantity deposits on the right-hand electrode from the concentrated solution, and  $u/(u+v)$  gram ion of M passes from the dilute to the concentrated solution and  $v/(u+v)$  gram ion of A passes from the concentrated to the dilute solution. The dilute solution gains, therefore,  $v/(u+v)$  gram ion each of M and A, and the concentrated solution loses the same quantities of these ions. Since the osmotic pressure of each kind of ion is reduced from  $P_2$  to  $P_1$ , the maximum work available is

$$A = 2 \frac{v}{u+v} RT \ln \frac{P_2}{P_1}$$

But the maximum work that can be accomplished during the passage of  $zF$  coulombs through the cell, from left to right, is given also by the equation

$$A = zFE$$

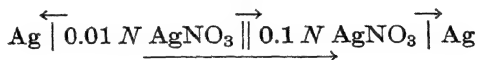
from which it follows that

$$\begin{aligned} E &= 2 \frac{v}{u+v} \frac{RT}{zF} \ln \frac{P_2}{P_1} \\ &= 2 \frac{v}{u+v} \frac{0.058}{z} \log \frac{P_2}{P_1} \end{aligned}$$

On replacing the osmotic pressures in this equation by the corresponding ionic concentrations, we obtain:

$$E = 2n_a \frac{0.058}{z} \log \frac{C_2}{C_1}$$

Values of the electromotive force of concentration cells, when calculated by means of equation 4, agree fairly closely with those determined by experiment, as shown by the following example. Abegg and Cumming<sup>1</sup> by direct measurement found the electromotive force of the cell



to be 0.0590 volt at 25°. Since the conductance ratio<sup>2</sup> of silver nitrate in 0.1 and 0.01 normal solution is 0.815 and 0.938, respectively, at 25°, and the transference number of the anion in silver nitrate is 0.54, the electromotive force of the cell, as calculated by equation 4, is

$$E = 2 \times 0.54 \times 0.059 \log \frac{0.0815}{0.00938} = 0.0598 \text{ volt}$$

When the potential difference at the junction of the two solutions is neglected,

$$E = 0.059 \log \frac{0.0815}{0.00938} = 0.0554 \text{ volt}$$

In making these calculations, it has been assumed that the ratio  $C_2/C_1$  is equal to the ratio  $\alpha_2 c_2 / \alpha_1 c_1$ , where  $\alpha$  is the conductance ratio of silver nitrate and  $c$  its concentration. We shall see, later, that this assumption is not strictly correct.

Although many measurements<sup>3</sup> have been made of the electromotive force of concentration cells containing non-aqueous solutions, it has not been possible, except in a few cases, to apply equation 4 to these cells, owing to the difficulty of obtaining reliable values for the concentrations of the ions in the solutions. Carrara and D'Agostino<sup>4</sup> showed that the equation is applicable to concentration cells containing methyl alcohol solutions, and Roshdestwensky and Lewis<sup>5</sup> found that the equation also holds for acetone solutions of silver nitrate. On the other hand, Gibbons

<sup>1</sup> *Z. Elektrochem.*, **13**, 18 (1907).

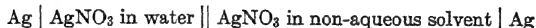
<sup>2</sup> Cf. Harkins, *J. Am. Chem. Soc.*, **33**, 1806 (1911).

<sup>3</sup> Cf. Jones, *Jahrb., Elektrochem.*, **1**, 38 (1894); Kahlenberg, *J. Phys. Chem.*, **4**, 709 (1900); Cady, *ibid.*, **9**, 477 (1906).

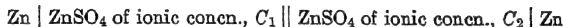
<sup>4</sup> *Atti ist. Veneto sci.*, **63**, 793 (1902).

<sup>5</sup> *J. Chem. Soc.*, **99**, 2138 (1911); **101**, 2094 (1912).

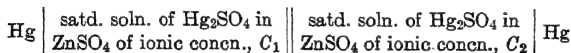
and Getman<sup>1</sup> found that equation 4 is not a true expression of all the factors which determine the potential differences in silver nitrate concentration cells of the type:



**Indirect Measurement of the Liquid-Liquid Potential Difference.** An ingenious method was employed by Cohen and Tombrock<sup>2</sup> for determining the liquid-liquid potential difference. The electromotive forces of the cells



and



were measured. The electromotive force of the first cell is given by the expression

$$E_1 = \frac{RT}{2F} \ln \frac{C_2}{C_1} + \pi_3$$

and that of the second cell, which is reversible with respect to the sulphate ion, by

$$E_2 = \frac{RT}{2F} \ln \frac{C_2}{C_1} - \pi_3$$

On subtracting these equations, we obtain,

$$\pi_3 = \frac{E_1 - E_2}{2} \quad (5)$$

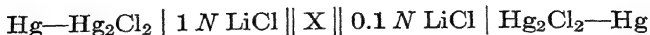
**Elimination of the Liquid-Liquid Potential Difference.** Various methods have been employed to eliminate (or reduce) the potential difference at the surface of contact of two solutions. A method due to Nernst consists in adding an indifferent salt to the solutions. The concentration of this salt, which is the same throughout the entire cell, is much higher than that of the other substances in the cell. This procedure was found<sup>3</sup> to reduce the potential difference at the interface to a very small value. Another method, more frequently employed, consists in placing a concentrated solution of a salt (called a "salt bridge") between the single electrodes. The mechanism of the effect of the salt bridge is

<sup>1</sup> *J. Am. Chem. Soc.*, **36**, 1630 (1914).

<sup>2</sup> *Z. Elektrochem.*, **13**, 612 (1907).

<sup>3</sup> Cf. Bugarszky, *Z. anorg. Chem.*, **14**, 145 (1897); Sackur, *Z. physik. Chem.*, **39**, 364 (1902).

obscure. The influence of various electrolytes in this connection was studied by Abegg and Cumming,<sup>1</sup> who measured the electromotive force of the cell



in which X denotes the electrolyte employed in the salt bridge. The values of the electromotive force obtained with different electrolytes are given in Table LVII.

TABLE LVII

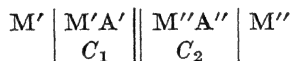
INFLUENCE OF A SALT BRIDGE ON THE ELECTROMOTIVE FORCE OF A CONCENTRATION CELL

X	E
0	0.0361 volt
1 <i>N</i> NH <sub>4</sub> NO <sub>3</sub>	0.0480 volt
5 <i>N</i> NH <sub>4</sub> NO <sub>3</sub>	0.0532 volt
10 <i>N</i> NH <sub>4</sub> NO <sub>3</sub>	0.0543 volt
Satd. KNO <sub>3</sub>	0.0502 volt
Satd. KCl	0.0515 volt

Since the sum of the electrode potentials of the cell is 0.0530 volt, it is evident that the intermediate solution largely eliminates the liquid-liquid potential difference. An extrapolation method for eliminating the potential difference at the junction of the two solutions has been described.<sup>2</sup>

Schatchard<sup>3</sup> showed that, in a hydrochloric acid concentration cell containing a saturated potassium chloride salt bridge, the liquid junction potential is not more than 1 millivolt for solutions having a concentration less than 0.1 molal, but that it increases rapidly with the concentration of the acid.

**Liquid Junction Potential Differences in Cells Containing More than Two Ions.** Equation 4 is applicable, of course, only to concentration cells containing one and the same binary salt (MA). We shall now consider a more complicated cell of the type



in which the ions have the same valence. The concentrations of the ions in the two solutions are represented by  $C_1$  and  $C_2$ . The liquid-liquid potential difference in this cell evidently depends on the velocities of

<sup>1</sup> *Z. Elektrochem.*, **13**, 17 (1907). Cf. Aten and Dalsen, *Rec. trav. chim.*, **45**, 177 (1926); Murray and Acree, *Bur. Standards J. Research*, **7**, 713 (1931).

<sup>2</sup> Owen, *J. Am. Chem. Soc.*, **60**, 2229 (1938).

<sup>3</sup> *Ibid.*, **45**, 1716 (1923).

four kinds of ions. Various expressions have been proposed for calculating the potential difference at the interface in cells of this type.

On the assumption that the boundary between the two solutions is initially sharp, Planck<sup>1</sup> deduced the expression

$$\pi_3 = \frac{RT}{zF} \ln \xi \quad (6)$$

where the transcendental function  $\xi$  is defined by the relation

$$\frac{\xi u_1 C_1 - u_2 C_2}{v_1 C_1 - \xi v_2 C_2} = \frac{\ln (C_1/C_2) - \ln \xi}{\ln (C_1/C_2) + \ln \xi} \cdot \frac{\xi C_1 - C_2}{C_1 - \xi C_2}$$

In the equation,  $C_1$  and  $C_2$  are the concentrations of the ions in the two solutions,  $u_1$  and  $u_2$  are the velocities of the cations, and  $v_1$  and  $v_2$  the velocities of the anions. Fales and Vosburgh<sup>2</sup> described a procedure for finding the value of  $\xi$ .

When the two salts have a mutual ion and the same concentration, equation 6 reduces to the form

$$\pi_3 = \frac{RT}{zF} \ln \frac{u_1 + v}{u_2 + v} \quad (7)$$

or

$$\pi_3 = \frac{RT}{zF} \ln \frac{u + v_1}{u + v_2} \quad (7a)$$

These equations, the validity of which was tested by Bjerrum,<sup>3</sup> are easily applied and give fairly accurate results.

On the assumption that the solutions are mechanically mixed at the boundary, Henderson<sup>4</sup> deduced the general expression

$$\pi_3 = \frac{RT}{F} \frac{(U_1 - V_1) - (U_2 - V_2)}{(U'_1 + V'_1) - (U'_2 + V'_2)} \ln \frac{(U'_1 + V'_1)}{(U'_2 + V'_2)} \quad (8)$$

where, in one solution,

$$U_1 = u_1 C_1 + u_2 C_2 + \dots$$

$$V_1 = v_1 C_1 + v_2 C_2 + \dots$$

$$U'_1 = u_1 z_1 C_1 + u_2 z_2 C_2 + \dots$$

$$V'_1 = v_1 z_1 C_1 + v_2 z_2 C_2 + \dots$$

and  $U_2$ ,  $V_2$ ,  $U'_2$ ,  $V'_2$  represent the corresponding sums in the other

<sup>1</sup> *Wied. Ann.*, **40**, 561 (1890).

<sup>3</sup> *Z. Elektrochem.*, **17**, 58 (1911).

<sup>2</sup> *J. Am. Chem. Soc.*, **40**, 1291 (1918).

<sup>4</sup> *J. physik. Chem.*, **59**, 118 (1906).

solution. This equation is not only easy to apply in practice, but it is the only equation which is applicable to cases where the ions have different valences ( $z$ ), without restriction of any kind.

In the preceding equations for the potential difference at the liquid-liquid junction, the velocities of the ions at zero concentration are used. The velocities of some ions, however, vary markedly with concentration. By employing ionic velocities corresponding to experimental concentrations, Cumming<sup>1</sup> showed that a considerable simplification of equation 8 is possible when the cation and anion of each salt have the same valence. Under these conditions equation 8 becomes (for solutions of single salts):

$$\pi_3 = \frac{RT}{F} \frac{C_1(u_1 - v_1) - C_2(u_2 - v_2)}{C_1 z_1(u_1 + v_1) - C_2 z_2(u_2 + v_2)} \ln \frac{C_1 z_1(u_1 + v_1)}{C_2 z_2(u_2 + v_2)} \quad (9)$$

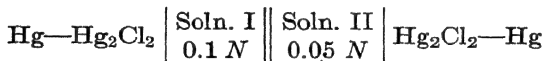
This expression may be simplified further by introducing the specific conductance of the solutions,  $\kappa = C(u + v)$ , and the transference number of the cations,

$$n_c = \frac{u}{u + v} \quad \text{or} \quad (u - v) = (u + v)(2n_c - 1)$$

When this is done, we obtain

$$\pi_3 = \frac{RT}{F} \frac{\kappa_1(2n_{c_1} - 1) - \kappa_2(2n_{c_2} - 1)}{\kappa_1 z_1 - \kappa_2 z_2} \ln \frac{\kappa_1 z_1}{\kappa_2 z_2} \quad (10)$$

Cumming employed equation 10 to calculate the liquid-liquid potential difference of a number of cells of the type



A few of his results, together with those determined experimentally by Henderson,<sup>2</sup> are given in Table LVIII. On the average the calculated values of  $E$  differ from the experimental values by 0.0011 volt.

For a concentration cell containing solutions of the same binary electrolyte, equation 10 becomes

$$\begin{aligned} \pi_3 &= \frac{RT}{zF} (2n_c - 1) \ln \frac{\kappa_1}{\kappa_2} \\ &= \frac{v - u}{u + v} \frac{RT}{zF} \ln \frac{\kappa_2}{\kappa_1} \end{aligned} \quad (11)$$

<sup>1</sup> *Trans. Faraday Soc.*, **8**, 86 (1912); **9**, 174 (1913).

<sup>2</sup> *Z. physik. Chem.*, **59**, 118 (1906).

which is identical with equation 3. When the two solutions have the same ionic concentration and one mutual ion, equation 10 becomes for univalent ions

$$\pi_3 = \frac{RT}{F} \ln \frac{A_1}{A_2} \quad (12)$$

Equation 12 had been deduced previously by Lewis and Sargent<sup>1</sup> for these special conditions. Values of the liquid-liquid potential between equiconcentrated solutions of a large number of univalent chlorides

TABLE LVIII

COMPARISON OF THE OBSERVED AND CALCULATED ELECTROMOTIVE FORCES OF CONCENTRATION CELLS

Solutions		Electrode Potentials Calculated by Equation 2	Calculated Liquid-Liquid Potential $\pi_3$	Calculated emf $E$	Observed emf $E$	Difference
0.1 N	0.05 N					
NaCl	KCl	0.0161	-0.0071	0.0090	0.0094	0.0004
KCl	NaCl	0.0169	0.0030	0.0199	0.0191	0.0008
KCl	LiCl	0.0171	0.0045	0.0216	0.0206	0.0010
LiCl	KCl	0.0158	-0.0108	0.0050	0.0063	0.0013
NaCl	LiCl	0.0169	-0.0027	0.0142	0.0124	0.0018
LiCl	NaCl	0.0161	-0.0081	0.0080	0.0092	0.0012

were measured by MacInnes and Yeh,<sup>2</sup> and, in most cases, the values obtained were found to be in excellent agreement with those calculated by means of equation 12.

A simple relation for the potential difference at the junction of differently concentrated solutions of the same salt, which involves no assumptions as to the concentrations of the ions in the two solutions, was deduced by MacInnes.<sup>3</sup> This relation may be expressed in the form

$$\pi_3 = E \left( 1 - \frac{1}{2n_c} \right) \quad (13)$$

**Flowing Junctions.** When the ions on the opposite sides of a liquid-liquid junction have markedly different velocities, it is difficult to obtain constant and reproducible potential differences at the interface. It has

<sup>1</sup> *J. Am. Chem. Soc.*, **31**, 363 (1909).

<sup>3</sup> *Ibid.*, **37**, 2301 (1915).

<sup>2</sup> *Ibid.*, **43**, 2563 (1921).



been found, however, that reproducible values may be obtained by renewing the surface of contact of the solutions. Walpole<sup>1</sup> accomplished this by forming the junction with tapes, along which the solutions were allowed to flow, and Lewis, Brighton, and Sebastian<sup>2</sup> employed an intermittent method for the same purpose.

Later, Lamb and Larson<sup>3</sup> developed a device, called a **flowing junction**, which produces a junction the surface of which is constantly renewed. By means of the flowing junction, potential differences can be obtained which are constant and reproducible within 0.00001 volt. This

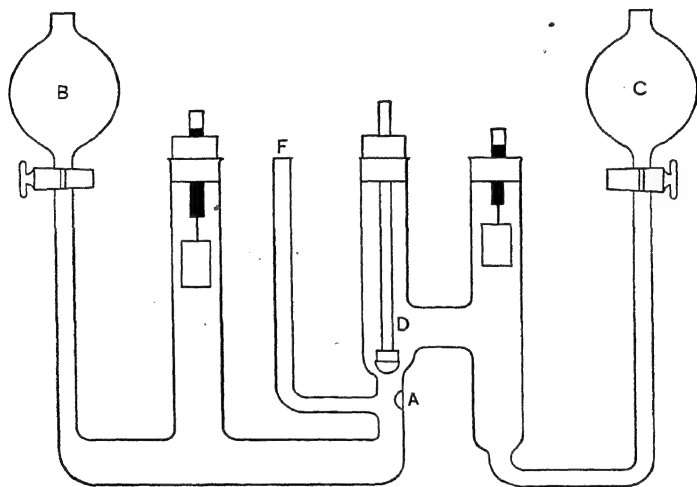


FIG. 66.

result is secured by having an upward current of the heavier solution meet a downward current of the lighter one at the point of union of a vertical tube with a horizontal outflow tube. A modification<sup>4</sup> of the Lamb and Larson flowing junction is shown in Fig. 66. The boundary, which forms at *A*, results from the meeting of two slowly moving solutions from the reservoirs *B* and *C*, the flow being regulated by a screw pinchcock on a rubber tube attached to the outflow tube *F*. By means of the glass rod *D*, which is tipped with rubber, it is possible to fill the reservoirs without mixing the solutions in the cell.

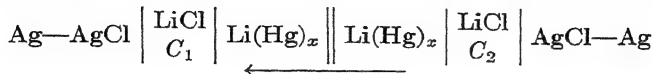
<sup>1</sup> *J. Chem. Soc.*, **105**, 2521 (1914).

<sup>2</sup> *J. Am. Chem. Soc.*, **39**, 2245 (1917).

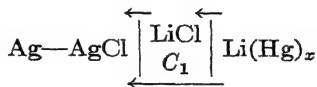
<sup>3</sup> *Ibid.*, **42**, 229 (1920).

<sup>4</sup> MacInnes and Yeh, *ibid.*, **43**, 2563 (1921).

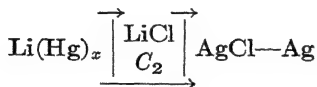
**Concentration Cells without Transference.** A less familiar type of concentration cell than those we have considered is one in which transference does not occur. In this kind of cell, the liquid junction is avoided by introducing an amalgam between the two solutions, as illustrated in the cell



This is really a double cell, formed by combining the single cells



and



Accordingly, the electromotive force of the double cell is equal to the sum of the electromotive forces of the single cells. This can readily be shown to be

$$E = \frac{2RT}{F} \ln \frac{C_2}{C_1} \quad (14)$$

if it is assumed the solutions are so dilute that one equivalent of lithium chloride functions as two moles, i.e., that the lithium chloride is completely dissociated. (Let the student derive equation 14.) Cells without transference were first investigated by Tolman and Ferguson,<sup>1</sup> MacInnes and Parker,<sup>2</sup> Chow,<sup>3</sup> MacInnes and Beattie,<sup>4</sup> and Knobel.<sup>5</sup>

It should be pointed out that, although the troublesome liquid-junction potential can be eliminated by constructing cells of this kind, it is difficult to find electrodes which are reversible to both ions of the electrolyte.

**Gas Electrodes.** Instead of employing amalgams of different concentrations, concentration cells in which the substances producing the ions are of different concentrations can be formed by combining gas electrodes in which the gas is at different concentrations or pressures. These electrodes were first studied extensively by Böttger,<sup>6</sup> Höber,<sup>7</sup> Wilshire,<sup>8</sup> Bose,<sup>9</sup> Czepinsky.<sup>10</sup>

<sup>1</sup> *J. Am. Chem. Soc.*, **34**, 232 (1912).

<sup>2</sup> *Ibid.*, **37**, 1445 (1915).

<sup>3</sup> *Ibid.*, **42**, 488 (1920).

<sup>4</sup> *Ibid.*, **42**, 1117 (1920).

<sup>5</sup> *Ibid.*, **45**, 70 (1923).

<sup>6</sup> *Z. physik. Chem.*, **24**, 253 (1897).

<sup>7</sup> *Z. anorg. Chem.*, **20**, 419 (1899).

<sup>8</sup> *Z. physik. Chem.*, **35**, 291 (1900).

<sup>9</sup> *Ibid.*, **34**, 701 (1900); **38**, 1 (1901).

<sup>10</sup> *Z. anorg. Chem.*, **30**, 1 (1902).

A gas electrode is formed by partially immersing in a solution of the ions of the gas a piece of platinum coated with some finely divided metal which absorbs the gas. The gas is then bubbled through the solution and allowed to surround the metal until the metal becomes saturated with it and the potential difference between the metal and the solution

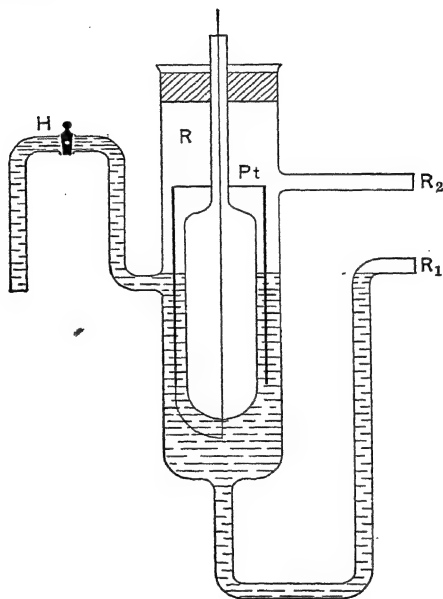


FIG. 67.

becomes constant. LeBlanc<sup>1</sup> showed that such an electrode is completely reversible and behaves like a metallic plate of the gaseous substance.

One of the most important electrodes of this kind is the hydrogen electrode. The reaction which takes place at the electrode is expressed by the equation



One form of hydrogen electrode is shown in Fig. 67. The glass vessel is half filled with acid which is normal with respect to hydrogen ions. A cylindrical platinum electrode (Pt) coated with platinum black is partially immersed in the solution of the acid and held in place by a well-

<sup>1</sup> *Z. physik. Chem.*, **12**, 333 (1893).

fitting rubber stopper. Electrical connection is made with the metal through a platinum wire sealed in the tube  $R$ . In order to saturate the electrode with hydrogen, a current of the gas is passed in through  $R_1$  and allowed to bubble through the solution for about thirty minutes, at the end of which time the exit tube,  $R_2$ , is closed.

A hydrogen concentration cell is formed by dipping the siphon tubes of two hydrogen electrodes in which the gas is at different pressures into

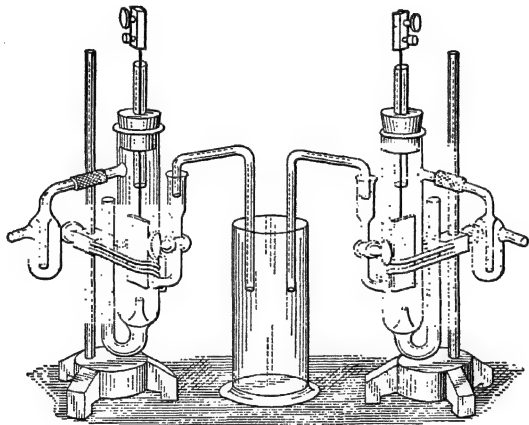


FIG. 68.

an intermediate vessel containing normal acid. Such a cell is shown in Fig. 68. When the cell produces electricity, hydrogen is ionized at one electrode and hydrogen ions are discharged at the other.

The calculation of the potential of a hydrogen electrode is similar to that for an amalgam electrode, except that it must be remembered that the hydrogen molecule contains two atoms. Hence, if  $p_1$  and  $p_2$  represent, respectively, the smaller and larger pressures of the gaseous hydrogen in the electrodes, the electromotive force of a hydrogen concentration cell is given by the expression

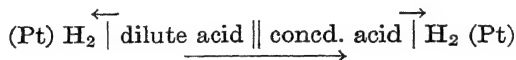
$$E = \frac{0.058}{2} \log \frac{p_2}{p_1} \quad (15)$$

Loomis, Myers, and Acree<sup>1</sup> found that equation 15 holds very closely over a range of pressures from 700 to 800 millimeters.

<sup>1</sup> *J. Phys. Chem.*, **21**, 334 (1917). Cf. Tammann and Diek, *Z. anorg. Chem.*, **150**, 129 (1926).

By the use of platinized platinum, reversible oxygen, chlorine, bromine, and iodine electrodes have been prepared. Bernfeld<sup>1</sup> studied a hydrogen sulphide electrode. A carbon monoxide cell was prepared by Hofmann and Wurthmann,<sup>2</sup> and a cell formed by combining a nitrogen with a calomel electrode was investigated by Usher and Venkateswaran.<sup>3</sup>

If the pressure of the gas in two hydrogen electrodes is the same, they may be combined to form a concentration cell in which the ions are at different concentrations, thus



In this cell it is necessary to keep the gas in each electrode at the same pressure while the electromotive force of the cell is being measured. This is best accomplished by allowing the gas to bubble slowly through the potential vessels while the measurement is being made, the stopcocks *H* (Fig. 67), being kept closed. If the stopcocks have not been coated with grease, electrical connection, usually sufficiently good to permit the passage of the current, is obtained by wetting them with the acid solution. If the connection is poor, the passage of the gas through the potential vessels must be discontinued and the stopcocks opened while the measurement is being made. The electromotive force of a hydrogen concentration cell of this type is given by equation 4.

**Applications of Potentiometric Measurements.** (*a*) *Determination of Transference Numbers.* A potentiometric method for the determination of transference numbers was first proposed by Helmholtz. It is evident from equation 4 that the transference numbers of the ions of an electrolyte may be determined by measuring the electromotive force of a concentration cell containing two solutions of the electrolyte, provided that the ionic concentrations are known. This knowledge is not necessary, however, if two concentration cells, one with and the other without transference, are constructed; for, on combining equations 4 and 14, we obtain

$$n_a = \frac{E_t}{E} \quad (16)$$

where  $E_t$  is the electromotive force of the cell with transference, and  $E$  that of the cell without transference. This equation permits the direct calculation of the transference number of the anion. The electromotive force method gives transference numbers for a definite concentration

<sup>1</sup> *Z. physik. Chem.*, **25**, 46 (1898).

<sup>2</sup> *Ber.*, **52**, 1185 (1919).

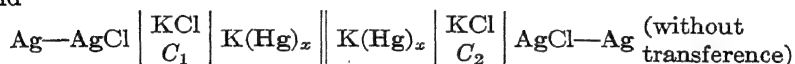
<sup>3</sup> *J. Chem. Soc.*, **115**, 613 (1919).

rather than mean values for a concentration range. At low concentrations, however, the method was found<sup>1</sup> to yield anomalous results. For cells reversible with respect to negative ions,  $n_a$  in equation 16 is replaced by  $n_c$ .

This method was employed by Pearce and Mortimer<sup>2</sup> and by MacInnes and Beattie<sup>3</sup> to determine the transference number of the lithium ion in lithium chloride, and by Knobel, Worcester, and Briggs<sup>4</sup> to determine that of the potassium ion in potassium hydroxide. The transference number of the potassium ion in potassium chloride was measured by MacInnes and Parker,<sup>5</sup> using cells constructed according to the schemes:



and



Their results, together with those obtained by other methods, are given in Table LIX.

TABLE LIX

TRANSFERENCE NUMBERS OF THE POTASSIUM ION IN POTASSIUM CHLORIDE

Concentration Ratio	$E_t$	$E$	Transference Numbers		
			$n_c = \frac{E_t}{E}$	Hittorf	Moving Boundary
0.5 : 0.05	0.05357	0.1074	0.498	0.496	.....
0.1 : 0.01	0.05400	0.1089	0.496	0.496	0.493
0.05 : 0.005	0.05470	0.11085	0.494	0.496	0.493

Ferguson and France<sup>6</sup> also employed an electrometric method to determine the transference numbers of the ions in sulphuric acid. The transference numbers of the ions in hydrogen chloride in methyl alcohol<sup>7</sup> and

<sup>1</sup> Wolfenden, Wright, Kane, and Buckley, *Trans. Faraday Soc.*, **23**, 491 (1927); Partington and Simpson, *ibid.*, **26**, 625 (1930).

<sup>2</sup> *J. Am. Chem. Soc.*, **40**, 518 (1918).

<sup>3</sup> *Ibid.*, **42**, 1117 (1920).

<sup>4</sup> *Ibid.*, **45**, 77 (1923).

<sup>5</sup> *Ibid.*, **37**, 1445 (1915).

<sup>6</sup> *Ibid.*, **43**, 2150 (1921).

<sup>7</sup> Nonhebel and Hartley, *Phil. Mag.*, **50**, 729 (1925).

in ethyl alcohol,<sup>1</sup> in lithium chloride in methyl alcohol,<sup>2</sup> in sodium iodide in ethyl alcohol,<sup>3</sup> and in potassium iodide in ethyl alcohol<sup>4</sup> were determined by the potentiometric method.

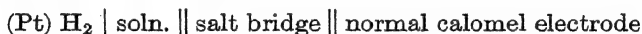
(b) *The Determination of Valence.* The valence of ions may be determined from electromotive force measurements by means of equation 2. The method may be illustrated by Ogg's<sup>5</sup> classical experiment. This experiment was carried out to ascertain whether the mercurous ion has the formula  $\text{Hg}^+$  or  $\text{Hg}_2^{++}$ , either of which is justified by the chemical behavior of mercurous salts. Ogg obtained a value of 0.029 volt at 17° for the electromotive force of a mercurous nitrate concentration cell, in which the ratio of the ionic concentrations was 0.5 : 0.05. Hence, since

$$z = \frac{0.058}{0.029} \log \frac{0.5}{0.05} = 2$$

the correct formula for mercurous nitrate is  $\text{Hg}_2(\text{NO}_3)_2$ . We may infer, therefore, that calomel has the formula  $\text{Hg}_2\text{Cl}_2$ .

In the same way, Reichinstein<sup>6</sup> determined the formula of potassium telluride to be  $\text{K}_2\text{Te}_2$ .

(c) *The Determination of Hydrogen-Ion Concentrations.* The hydrogen electrode is very frequently employed to determine the hydrogen-ion concentration of solutions. A hydrogen electrode is formed with the solution in question, and this is combined with a normal calomel electrode, according to the scheme



The electromotive force of this cell is then measured. If the electrode potentials of the cell are referred to that of the normal hydrogen electrode as zero, we have the following relation between the electromotive force of the cell and the hydrogen-ion concentration ( $C_{\text{H}}$ ) of the solution:

$$E = \frac{RT}{F} \ln \frac{1}{C_{\text{H}}} + 0.281 \quad (17)$$

<sup>1</sup> Woolcock, Hartley, and Hughes, *Phil. Mag.*, **11**, 222 (1931); cf. Harned and Fleysher, *J. Am. Chem. Soc.*, **47**, 92 (1925).

<sup>2</sup> Pearce and Hart, *J. Am. Chem. Soc.*, **44**, 2411 (1922).

<sup>3</sup> Partington and Simpson, *Trans. Faraday Soc.*, **26**, 625 (1930).

<sup>4</sup> Partington and Isaacs, *ibid.*, **25**, 53 (1929).

<sup>5</sup> *Z. physik. Chem.*, **27**, 285 (1898).

<sup>6</sup> *Ibid.*, **97**, 257 (1921).

Following the suggestion of Sørensen,<sup>1</sup> most biologists and biochemists now express hydrogen-ion concentrations in terms of  $\log \frac{1}{C_H} = \text{pH}$ . Thus,  $\text{pH} = 6$  is equivalent to  $[H^+] = 10^{-6}$ . While  $[H^+]$  values diminish with decreasing acidity, the corresponding  $\text{pH}$  values increase.

(d) *Potentiometric Titration*. Since the neutralization of an acid involves a change in hydrogen-ion concentration, it is evident from what has been said that the indicator employed in the titration of an acid may be replaced by a hydrogen electrode. The application of this electrode to titration was first made by Böttger,<sup>2</sup> but his method involved a considerable loss of time in making adjustments and calculations. Later, Hildebrand<sup>3</sup> developed a quicker and simpler method, in which the potentiometer employed by Böttger was replaced by a voltmeter. This method is briefly as follows:

The solution of acid is placed in a beaker (Fig. 69) which contains a hydrogen electrode *h* and the side tube of a normal calomel electrode *C*. The two electrodes are connected to the battery *B*, the calomel electrode through an electrometer or galvanometer *E*. The electromotive force of the cell, hydrogen electrode-calomel electrode, is balanced against a variable fraction of the electromotive force of the battery *B* by moving the sliding contact *S* along the resistance *ab* until, on depressing the key *K*, the electrometer does not give a deflection. The fall of potential from *a* to *S* is given by the voltmeter *V*, and when a balance is attained this is equal to the electromotive force of the cell. Since in a neutral solution the concentration of the hydrogen and hydroxyl ions is each  $10^{-7}$  (see Chapter XVIII), the "end point" is reached in the neutralization of a strong acid by a strong base when, at 25°, the electromotive force of the above cell, and therefore the reading on *V*, is

$$E = 0.059 \log \frac{1}{10^{-7}} + 0.281 = 0.694 \text{ volt}$$

In order to determine the amount of acid in the solution, a solution of standardized alkali is run into the beaker and the electromotive force of the cell measured from time to time. The solution of the alkali is added slowly to the beaker until the voltmeter reading is 0.694 volt; or else the quantity of alkali required to neutralize the acid is determined by plotting a number of voltmeter readings against the corresponding volumes

<sup>1</sup> *Études enzymatique*, II, 1909. See also Clark, *Determination of Hydrogen Ions*, 1928.

<sup>2</sup> *Z. physik. Chem.*, **24**, 253 (1895).

<sup>3</sup> *J. Am. Chem. Soc.*, **35**, 847 (1913).



of standardized alkali added to the solution of the acid, and finding from the curve the volume corresponding to 0.694 volt.

Some of the results obtained by Hildebrand are illustrated by the curves in Fig. 70. It will be noted that the curves show a sharp break near the neutral point, which is indicated by the dotted line. Above this line the solution becomes increasingly alkaline, and below it increasingly acid.

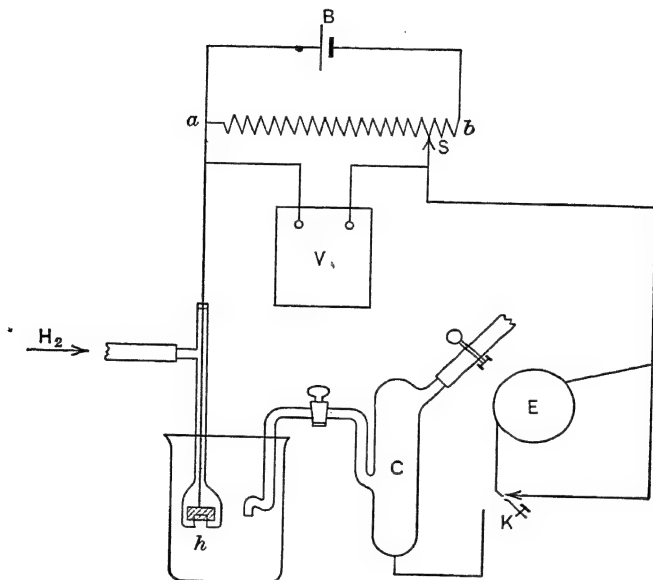


FIG. 69.

A solution may be titrated to a particular hydrogen-ion concentration as follows: The solution is placed in an electrode vessel with a hydrogen electrode, and a solution having the desired hydrogen-ion concentration is placed in a second similar vessel, also having a hydrogen electrode. The two vessels are then connected through a sensitive galvanometer and tapping key, and the titrating solution is slowly run into the first solution until, on depressing the key, the galvanometer gives no deflection. Solutions (buffer solutions, see p. 351) having a wide range of  $pH$  values may be readily prepared by mixing 0.2  $M$  disodium phosphate and 0.1  $M$  citric acid combined in such volumes as to give 20 cc of the mixture. Hydrogen-ion concentrations that may be obtained in this

way are given in Table LX.<sup>1</sup> Other standard solutions having a still wider range of pH values than those given in Table LX have been described by Sørensen, Walpole, Clark and Lübs, and others.<sup>2</sup>

The potentiometric method of titration is more rapid than the indicator, or colorimetric, method. It is especially applicable to highly

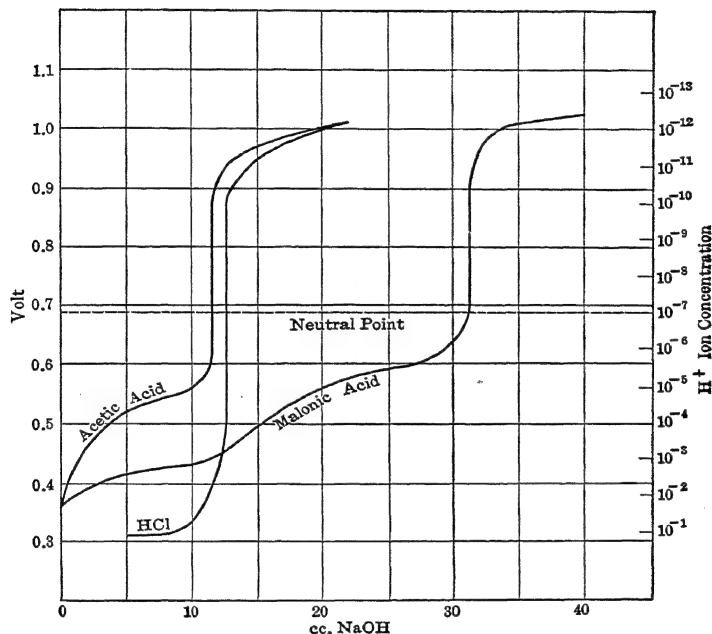


FIG. 70.

colored and turbid solutions, and titrations are frequently possible in complex mixtures in which indicator color changes are indefinite. By means of the potentiometric method it is often possible to obtain information that cannot be secured by the indicator method. For example, not only can the total acidity be determined, but also the acidity at every point and frequently the nature and number of acids can be ascertained. The method is adapted to the control of many industrial processes.<sup>3</sup>

<sup>1</sup> McIlvaine, *J. Biochem.*, **49**, 183 (1921).

<sup>2</sup> Clark, *Determination of Hydrogen Ions*, pp. 69-83, 1928.

<sup>3</sup> Cf. Keeler, *J. Ind. Eng. Chem.*, **14**, 395 (1922); Klopsteg, *ibid.*, **14**, 399 (1922).

TABLE LX

COMPOSITION OF SOLUTIONS HAVING PARTICULAR HYDROGEN-ION  
CONCENTRATIONS

<i>pH</i> Required	Number of cc of:	
	0.2 <i>M</i> $\text{Na}_2\text{HPO}_4$	0.1 <i>M</i> Citric Acid
2.2	0.40	19.60
2.4	1.24	18.76
2.6	2.18	17.82
2.8	3.17	16.83
3.0	4.11	15.89
3.2	4.94	15.06
3.4	5.70	14.30
3.6	6.44	13.56
3.8	7.10	12.90
4.0	7.71	12.29
4.2	8.28	11.72
4.4	8.82	11.18
4.6	9.35	10.65
4.8	9.86	10.14
5.0	10.30	9.70
5.2	10.72	9.28
5.4	11.15	8.85
5.6	11.60	8.40
5.8	12.09	7.91
6.0	12.63	7.37
6.2	13.22	6.78
6.4	13.85	6.15
6.6	14.55	5.45
6.8	15.45	4.55
7.0	16.47	3.53
7.2	17.39	2.61
7.4	18.17	1.83
7.6	18.73	1.27
7.8	19.15	0.85
8.0	19.45	0.55

Many forms of apparatus have been described,<sup>1</sup> and potentiometric titration has been extensively studied,<sup>2</sup> particularly for the purpose of extending the method to oxidation-reduction titrations and to titrations in which a slightly soluble substance is formed. Indeed, most of the reactions employed in volumetric analysis can be studied by the potentiometric method.<sup>3</sup>

The success of potentiometric titration depends on the fact that near the end point there is a rapid change in the concentration of the substance being titrated or of the titrant, and this gives rise to a rapid change in the potential of the electrode. Accordingly, if the electromotive force  $E$  of the cell is plotted against the volume  $v$  of the titrant added, the end point, or equivalence point, corresponds to the maximum slope  $\Delta E/\Delta v$  of the curve when the reaction is one between a strong acid and a strong base, one in which a slightly soluble salt of the symmetrical valence type is formed,<sup>4</sup> or a fairly complete oxidation-reduction. In the neutralization of a weak acid by a strong base, for example, at the point for which  $\Delta E/\Delta v$  is a maximum the hydrogen-ion concentration is greater than that at the equivalence point by  $0.65\sqrt{k_w/ck_a}$ , where  $c$  is the concentration of the acid and  $k_a$  and  $k_w$  are the dissociation constant (see Chapter XIII) of the acid and the ionic product of water (see Chapter XVIII), respectively.<sup>5</sup> When the highest accuracy is desired the equivalence point may be calculated from several potentials determined during the course of the titration.<sup>6</sup>

The nature of the titration determines the kind of indicator electrode

<sup>1</sup> Cf. Bartell, *J. Am. Chem. Soc.*, **39**, 630 (1917); Robbins, *ibid.*, **39**, 646 (1917); Bovie, *ibid.*, **44**, 2892 (1922); Sharp and MacDougall, *ibid.*, **44**, 1193 (1922); Waters, *J. Soc. Chem. Ind.*, **41**, 3371 (1922); Callan and Horrobin, *ibid.*, **47**, 329T (1928); Clarke and Wooten, *Ind. Eng. Chem., Anal. Ed.*, **3**, 402 (1931); Wilcox, *ibid.*, **4**, 38 (1932). The application of the electron tube to potentiometric titrations is described by Williams and Whitenack, *J. Phys. Chem.*, **31**, 519 (1927); cf. also Jolibois and Fourteter, *Compt. rend.*, **194**, 872 (1932).

<sup>2</sup> See, for example, Treadwell and Weiss, *Helv. Chim. Acta*, **2**, 680 (1919); **3**, 433 (1920); Kolthoff, *Rec. trav. chim.*, **39**, 280 (1922); **41**, 343 (1922); *Z. anorg. Chem.*, **112**, 155 (1920); *Z. anal. Chem.*, **61**, 369 (1922); Auerbach and Smolczyk, *Z. physik. Chem.*, **110**, 65 (1924). The last paper discusses the theory and practice of electro-metric titration.

<sup>3</sup> A large number of processes has been listed by Kolthoff and Furman, *Potentiometric Titrations*, 1931; Ellis and Fox, *Chem. Soc. Ann. Repts.*, **27**, 227 (1930); Glasstone, *ibid.*, **30**, 293 (1933).

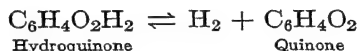
<sup>4</sup> Eastman, *J. Am. Chem. Soc.*, **47**, 332 (1925).

<sup>5</sup> Roller, *ibid.*, **50**, 1 (1928); **54**, 3485 (1932).

<sup>6</sup> Cf. Hahn and co-workers, *Z. physik. Chem.*, **127**, 1 (1927); **A146**, 363, 373 (1930); **A157**, 203, 206, 209 (1931); Cavanagh, *J. Chem. Soc.*, **1930**, 1425; Fenwick, *Ind. Eng. Chem., Anal. Ed.*, **4**, 144 (1932).

employed in potentiometric titration. When the titration involves an oxidation-reduction reaction smooth platinum is commonly used; for precipitation reactions the indicator electrode generally consists of the metal of the slightly soluble salt. For neutralizations some form of hydrogen electrode is employed.

*The Quinhydrone Electrode.* When quinhydrone<sup>1</sup> (an equimolecular compound of quinone and hydroquinone) is dissolved in water, it decomposes into its components and gives a definite hydrogen partial pressure which is regulated by the equilibrium



In consequence of this the hydrogen of the platinum-hydrogen electrode may be replaced by the addition of quinhydrone to the solution to be tested. The quinhydrone electrode<sup>2</sup> formed in this way has a constant and reproducible potential, which depends only upon the hydrogen-ion concentration and which changes, with variation in the hydrogen-ion concentration, in exactly the same way as that of the hydrogen electrode (see p. 233). The following values, referred to the normal hydrogen electrode, have been obtained for the potential of the quinhydrone electrode:

0.005 <i>M</i> quinhydrone	0.7044 volt (18°)
0.005 <i>M</i> quinhydrone	0.6990 volt (25°)
0.005 <i>M</i> quinhydrone + hydroquinone	0.6185 volt (18°)
0.005 <i>M</i> quinhydrone + quinone	0.7570 volt (18°)

The salt error of the electrode was determined by Sørensen and Linderström-Lang.<sup>3</sup> The quinhydrone electrode may be used for determination of hydrogen-ion concentrations in solutions the *pH* value of which is between 1 and 8. In alkaline solutions (*pH* greater than 8), the electrode does not give reliable results, owing to the formation of a brown-colored weak acid.

On account of its greater ease of manipulation, the quinhydrone electrode is being employed more and more as a substitute for the hydrogen

<sup>1</sup> Pure quinhydrone can easily be prepared by mixing alcoholic solutions of hydroquinone and quinone in equimolecular proportions and pouring the mixture into cold water.

<sup>2</sup> Cf. Büllmann, *Ann. chim. phys.*, [ix] **15**, 109 (1921); *Trans. Faraday Soc.*, **19**, 57 (1923); Büllmann and Lund, *Ann. chim. phys.*, [ix] **16**, 321 (1921); Büllmann and Krarup, *J. Chem. Soc.*, **125**, 1954 (1924).

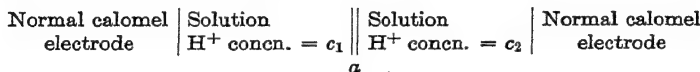
<sup>3</sup> *Ann. chim. phys.*, [ix] **15**, 111 (1921); Linderström-Lang, *Compt. rend. trav. Lab. Carlsberg*, **15**, No. 4 (1924).

electrode.<sup>1</sup> To carry out a titration, it is only necessary to add some quinhydrone to the solution and to dip in a bright platinum or gold electrode. Not only is the electrode more easily prepared, but it possesses many advantages over the hydrogen electrode. For example, its potential is more quickly established, and, in consequence, electrical stirring is usually unnecessary; it can be used in solutions containing metallic salts and alkaloids, in which the hydrogen electrode is useless.

*The Antimony Electrode*,  $\text{Sb} \mid \text{Sb}_2\text{O}_3$ . Considerable attention has been directed to this practical and useful hydrogen-ion indicator. Since the surface of the cast metal is coated with a thin layer of the oxide, theoretically it behaves as an oxygen electrode the potential of which depends upon the hydrogen-ion concentration of the solution.<sup>2</sup> This electrode, which may be used without the addition of oxide to the solution,<sup>3</sup> gives a correct measure of hydrogen-ion concentrations from pH 2.2 to 7.8 inclusive, but outside of this range it does not function satisfactorily.<sup>4</sup> It is not readily poisoned.<sup>5</sup> The value of the electromotive force with this electrode, measured against the normal calomel electrode at 25°, is given by the equation <sup>6</sup>

$$E = 0.030 + 0.0591 \text{ pH} \quad (18)$$

*The Glass Electrode*. Although, some time ago, it was found <sup>7</sup> that the potential difference between two solutions separated by a glass plate depended on their hydrogen-ion concentrations, more than a decade elapsed before the glass electrode was employed <sup>8</sup> as a hydrogen-ion indicator. In a cell of the type



<sup>1</sup> Cf. Kolthoff, *Rec. trav. chim.*, **42**, 186 (1923); LaMer and Parsons, *J. Biol. Chem.*, **57**, 613 (1923); Harris, *J. Chem. Soc.*, **123**, 3924 (1923); Auerbach and Smoleczyk, *Z. physik. Chem.*, **110**, 65 (1924); Niklas and Hock, *Z. angew. Chem.*, **38**, 407 (1925); Wagener and McGill, *J. Am. Pharm. Assoc.*, **14**, 288 (1925); Hetterschij and Hudig, *Chem. Weekblad*, **23**, 2 (1926); Dawson, *Sugar*, **28**, 211, 262, 310 (1926); Lammert and Morgan, *J. Am. Chem. Soc.*, **54**, 910 (1932).

<sup>2</sup> Kolthoff and Hartong, *Rec. trav. chim.*, **44**, 113 (1925).

<sup>3</sup> Franke and Williams, *Ind. Eng. Chem.*, **20**, 87 (1928).

<sup>4</sup> Parks and Beard, *J. Phys. Chem.*, **37**, 821, 822 (1933); *J. Am. Chem. Soc.*, **54**, 856 (1933). The second paper gives an excellent summary of investigations carried out with the antimony electrode; see also Kauko and Knappsberg, *Z. Elektrochem.*, **45**, 760 (1939).

<sup>5</sup> Catenacci, *Intern. Sugar J.*, **34**, 185 (1932).

<sup>6</sup> Parks and Beard, *loc. cit.*

<sup>7</sup> Haber and Klemensiewicz, *Z. physik. Chem.*, **67**, 385 (1909).

<sup>8</sup> Cf. Hughes, *J. Am. Chem. Soc.*, **44**, 2860 (1922); *J. Chem. Soc.*, **1928**, 491; MacInnes and Dole, *Ind. Eng. Chem., Anal. Ed.*, **1**, 57 (1928).

the potentials of the two calomel electrodes cancel one another, and the electromotive force of the cell is equal to the potential difference at the glass membrane,  $a$ . Provided that there is no potential, in this membrane,

$$E = \frac{RT}{F} \ln \frac{c_2}{c_1} \quad (19)$$

If either  $c_1$  or  $c_2$  is known the other can be calculated. However, owing to differences in the surfaces of the glass membrane, a small correction must be made for "asymmetry potential" due to the glass. This correction can be ascertained by determining the electromotive force of the cell when the hydrogen-ion concentrations of both solutions are known or equal.

The theory of the glass electrode has been discussed frequently, and mechanisms have been proposed to explain its action. Dole<sup>1</sup> demonstrated that it does not behave as a semi-permeable membrane. The assumption of Horowitz,<sup>2</sup> that the glass electrode behaves as a hydrogen electrode on account of the ability of the glass to exchange sodium ions for hydrogen ions, has received both theoretical and experimental support.<sup>3</sup> According to Haugaard,<sup>4</sup> the sodium ion is quantitatively responsible for the transfer of the electricity through the glass. Haugaard gives the following picture of what occurs when the glass electrode comes in contact with an acid, neutral, or weakly basic solution: "At first the glass will take up water and the sodium salt of silicic acid will dissociate under the influence of the water taken up, hydrogen ions at the same time being absorbed,—in other words, the sodium salt of the weak silicic acid is partially hydrolyzed at the surface by the water, forming in the surface layer a skeleton of silicic acid. Hydrogen ions react readily with this surface, which affords an easy entrance of the hydrogen ions into the glass. In the middle of the glass there is a layer of intact sodium salt. With the passage of feeble currents through the membrane during the compensation of the electromotive force of the system, there will be a slight movement of the salt layer toward one side, depending on the direction of the current."

The glass electrode is particularly convenient for determining the hydrogen-ion concentration in very small amounts of liquid<sup>5</sup> and under

<sup>1</sup> *J. Am. Chem. Soc.*, **53**, 4260 (1931).

<sup>2</sup> *Z. Physik*, **15**, 369 (1932).

<sup>3</sup> MacInnes and Belcher, *J. Am. Chem. Soc.*, **53**, 3315 (1931); Gross and Halpern, *J. Chem. Phys.*, **2**, 136 (1934); Nikolski, *J. Phys. Chem. Russ.*, **10**, 495, 504, 513 (1937); Haugaard, *Nature*, **140**, 66 (1937); *J. Phys. Chem.*, **45**, 148 (1941).

<sup>4</sup> *Loc. cit.*, 1941.

<sup>5</sup> MacInnes and Dole, *J. Gen. Physiol.*, **12**, 805 (1929).

conditions which make the hydrogen electrode useless, as in the presence of oxidizing agents; it is most satisfactory for the automatic control of hydrogen-ion concentration during the growth of acid-forming bacteria.<sup>1</sup> With this electrode *pH* may be measured within 0.03 unit at temperatures up to 60°. <sup>2</sup> If corrections are made for asymmetry potential, the hydrogen and glass electrodes agree to  $\pm 0.0002$  volt from *pH* 2 to 8; <sup>3</sup> above and below these limits the error with the glass electrode corresponds to about 0.1 *pH*. A disadvantage of the electrode is the very high internal resistance (5–200 megohms) which it introduces into the cell, thereby necessitating the use of a quadrant electrometer or a vacuum-tube voltmeter to determine the electromotive force of the cell.<sup>4</sup>

In the preparation of the electrode, a glass containing 72 per cent  $\text{SiO}_2$ , 22 per cent  $\text{Na}_2\text{O}$ , and 6 per cent  $\text{CaO}$  is recommended.<sup>5</sup> A small piece of this glass is melted into the end of a Pyrex tube having a diameter of 4 millimeters, and then blown out in the form of a bubble until interference fringes show. While still soft, this bubble is pressed flat to form a diaphragm on the end of the tube.<sup>6</sup>

(e) *Miscellaneous Applications.* The electromotive force measurement of a concentration cell affords a convenient and accurate method for the determination of amounts of substances ranging from minute traces to low percentages, provided that the substances are capable of affecting the electrodes in a reversible manner. Using silver chloride electrodes, Furman and Low <sup>7</sup> employed such a method for the estimation of the small quantities of chloride which are present as impurities in salts, and measured accurately traces of chloride of a concentration as low as 0.00035 gram  $\text{Cl}^-$  per liter.

In view of the difficulties encountered in exact calorimetric measurements, it is not surprising that electromotive force data for concentration cells have been used to evaluate heats of dilution by means of the Gibbs-Helmholtz equation.<sup>8</sup>

<sup>1</sup> Longworth and MacInnes, *J. Bact.*, **29**, 595 (1935); **31**, 287, **32**, 567 (1936).

<sup>2</sup> Smirnov, *J. Gen. Chem. Russ.*, **7**, 796 (1937).

<sup>3</sup> MacInnes and Belcher, *J. Am. Chem. Soc.*, **53**, 3315 (1931).

<sup>4</sup> For details of the use of the glass electrode, see Daniels, Mathews, and Williams, *Experimental Physical Chemistry*, p. 205, 1941.

<sup>5</sup> MacInnes and Dole, *J. Am. Chem. Soc.*, **52**, 29 (1930).

<sup>6</sup> Glass electrodes are now manufactured by Leeds and Northrup, Philadelphia, Pa.

<sup>7</sup> *J. Am. Chem. Soc.*, **57**, 1585 (1935).

<sup>8</sup> Cf. Harned and co-workers, *ibid.*, **57**, 27 (1935); **58**, 496, 989, 2624 (1936); **59**, 360, 1280 (1937); LaMer and Carpenter, *J. Phys. Chem.*, **40**, 287 (1936). For a discussion of methods, see Glasstone, *Chem. Soc. Ann. Repts.*, **1937**, 92.

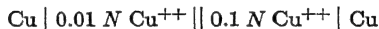


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 DOLE, *The Glass Electrode*, 1941.

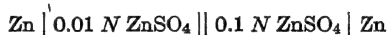
## PROBLEMS

1. Calculate the electromotive force of the cell



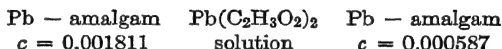
being given that the transference number of the copper ion in the electrolyte is 0.38.

2. The electromotive force of the cell



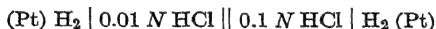
is 0.0275 volt. Given that the conductances of the zinc and sulphate ions are 47 and 70, respectively, calculate the ratio of the ionic concentrations.

3. Calculate the electromotive force of the cell



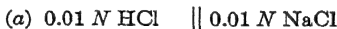
4. Two hydrogen electrodes are combined by means of an intermediate solution. What is the electromotive force of the cell when the pressure of the gas in the first electrode is 760 mm, that in the second electrode is 400 mm, and the temperature is 18°?

5. Calculate the electromotive force of the cell

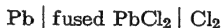


being given that the effective ion concentrations in the dilute and concentrated solutions are 0.00924 and 0.0814, respectively, and that the conductances of the hydrogen and chlorine ions are 313 and 65.3.

6. At 25°, what are the potential differences at the junctions:



7. At  $t^\circ \text{C}$ . the electromotive force of the cell



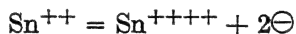
is given by the expression  $1.263 - [0.000679(t - 498)]$  volts. Calculate the heat of formation of lead chloride at 598° C.

8. What cells would you construct in order to obtain the heat of the change  $2 \text{ N HCl} \rightarrow 1 \text{ N HCl}$ ?

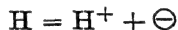
## CHAPTER X

### ELECTROMOTIVE FORCE OF OXIDATION-REDUCTION CELLS

According to modern ideas, oxidation occurs not only when oxygen is added to a substance, but also whenever electrons are withdrawn from its molecules, atoms, or ions. Similarly, reduction consists in the addition of negative electricity to the molecules, atoms, or ions of a substance. Thus, the oxidation of a stannous to a stannic salt may be represented by the equation



the oxidation of the element hydrogen by the equation

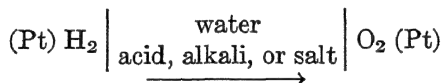


and the reduction of a ferricyanide to a ferrocyanide by the equation



Since the metals are capable of forming only positive ions, they can act only as reducing agents. On the other hand, all elements which produce only negative ions function solely as oxidizing agents.

**Oxidation-Reduction Cells.** One of the most important reversible gas cells is the hydrogen-oxygen cell, in which the (Pt) electrodes are saturated with hydrogen and oxygen, respectively. This cell may be represented as follows:



When a current is produced by this cell, hydrogen ionizes at the left-hand electrode, while at the right-hand electrode oxygen ionizes and unites with the water to form hydroxyl ions, in accordance with the equation



Theoretically, only water is necessary as the electrolyte, but acid, alkali, or salt is added to increase the conductance. The electromotive force of the cell is independent, however, of the nature of the electrolyte. The

theoretical value of the electromotive force of the hydrogen-oxygen cell, as calculated from the free energy of the formation of water from its constituents, is 1.23 volts (see Chapter VIII). The actual values are smaller than this, probably owing to the formation of platinum oxide, the potential difference of which is different from that of pure oxygen.

It is evident that the hydrogen-oxygen cell may be regarded as an **oxidation-reduction cell**. When the cell produces electricity, hydrogen is oxidized at the left-hand electrode, i.e.,

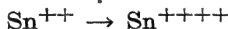


and oxygen is reduced at the other



For the same reasons a hydrogen-chlorine cell is an oxidation-reduction cell, hydrogen being oxidized at one electrode and chlorine reduced at the other.

By means of electromotive force measurements, it is possible to determine the tendency of an ion to pass from a lower to a higher state of oxidation; e.g.,



Such measurements may be accomplished by the use of platinized platinum electrodes, a cell being constructed in accordance with the scheme



If the left-hand electrode is connected with the positive pole of a storage battery and the right-hand electrode with the negative pole, the stannous ions in the left half of the cell will each give up two electrons to the electrode and become stannic ions, while the stannic ions in the right half of the cell will be reduced to stannous ions by taking up electrons. If the platinum electrodes, instead of being connected with the poles of a storage battery, are joined together by a wire, thus:



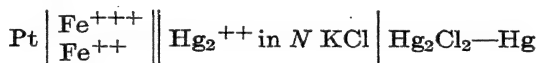
the same process occurs. The stannous ions each give up two electrons to the left-hand electrode, thereby becoming stannic ions. These electrons flow along the wire to the right-hand electrode where they are acquired by the stannic ions, which are thereby converted into stannous ions. This process continues until the ratio  $[\text{Sn}^{++}] \mid [\text{Sn}^{++++}]$  is the same for both solutions, when equilibrium sets in.

<sup>1</sup> Cf. Ostwald, *Z. physik. Chem.*, **15**, 399 (1894).

If a platinized platinum electrode is immersed in a solution containing stannous ions, and another in a solution containing ferric ions, and the two electrodes are combined to form a cell, then, on joining the electrodes by a wire, a current is produced which passes through the cell from the stannous to the ferric solution. Here the stannous ions give up electrons while the ferric ions take up electrons.

Although at first sight the oxidation of one ion by another at a distance may appear puzzling, this phenomenon is readily understood in the light of the previous discussion. The essential feature of the phenomenon is the transfer of a portion of the electrons of the ions in the lower state of oxidation, through the wire connecting the electrodes, to those in the higher state of oxidation.

**Oxidation Potential.** In order that we may obtain a relation between the electromotive force of oxidation-reduction cells and the tendency of the components to pass from a lower to a higher state of oxidation (oxidation) or from a higher to a lower state of oxidation (reduction), let us consider the cell



The reaction which takes place in the cell may be represented by the equation



the direction of the reaction depending upon the relative concentrations of the reacting substances.

The equilibrium constant of the foregoing reaction is

$$K' = \frac{[\text{Fe}_e^{++}]^2 [\text{Hg}_{2e}^{++}]}{[\text{Fe}_e^{+++}]^2 [\text{Hg}_e]^2}$$

where the subscript *e* denotes the equilibrium concentrations. In accordance with equation 21, Chapter VIII, the maximum work available from the reaction is

$$A = RT \ln K' - RT \ln \frac{[\text{Fe}^{++}]^2 [\text{Hg}_2^{++}]}{[\text{Fe}^{+++}]^2 [\text{Hg}]^2} \quad (1)$$

Since for one mole of mercury oxidized we also have

$$A = 2FE$$

where *E* is the electromotive force of the cell, it follows that

$$E = \frac{RT}{2F} \ln K - \frac{RT}{2F} \ln \frac{[\text{Fe}^{++}]^2 [\text{Hg}_2^{++}]}{[\text{Fe}^{+++}]^2 [\text{Hg}]^2} \quad (2)$$

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Further, since the concentrations of the mercury and the mercurous ions are constant, we may write

$$E = \frac{RT}{2F} \ln K - \frac{RT}{F} \ln \frac{[\text{Fe}^{++}]}{[\text{Fe}^{+++}]}$$
 (3)

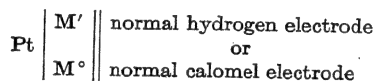
where

$$K = \frac{[\text{Fe}_e^{++}]^2}{[\text{Fe}_e^{+++}]^2}$$
 (4)

Setting  $\frac{RT}{2F} \ln K = E_0$ , we obtain:

$$E = E_0 - \frac{RT}{F} \ln \frac{[\text{Fe}^{++}]}{[\text{Fe}^{+++}]}$$
 (5)

For any cell,



equation 5 can be written in the general form

$$E_{(C^\circ \leftarrow C')} = E_0 - \frac{RT}{nF} \ln \frac{C^\circ}{C'}$$
 (6)

where  $E_{(C^\circ \leftarrow C')}$  is the electromotive force produced by the change of the ions from a higher state of oxidation ( $\text{M}'$ ) to a lower state of oxidation ( $\text{M}^\circ$ );  $C^\circ$  and  $C'$  are the ionic concentrations in the lower and higher states of oxidation;  $E_0$  is the electromotive force of the cell when  $C^\circ$  is equal to  $C'$ , and  $n$  is the difference in the valences of the ions. The electromotive force  $E$  is called the **oxidation potential**, and  $E_0$  is termed

the **normal oxidation potential**, of the electrode  $\text{Pt} \left| \begin{array}{c} \text{M}' \\ \text{M}^\circ \end{array} \right|$ . These quantities

are a measure of the tendency of an ion to pass from a higher to a lower state of oxidation. A positive value for the oxidation potential of an electrode means that positive electricity flows from right to left inside a cell *arranged as above*. Accordingly,  $\text{M}'$  is reduced and hydrogen or mercury is oxidized. The more positive the value of the oxidation potential, the more effective is the ion in the higher state of oxidation as an oxidizing agent; conversely, the more negative the oxidation potential, the more powerful is the ion in the lower state of oxidation as a reducing agent. In general, a solution which gives an indifferent electrode,  $\text{Pt} | \text{solution}$ , a positive potential difference will oxidize any other solution which gives to the electrode a lower positive potential difference.

Since the potential difference of the electrode  $\text{Pt} \left| \begin{array}{c} \text{MnO}_4^- \\ \text{acid} \end{array} \right|$  has a high

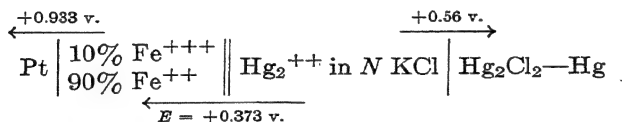
positive value, and that of the electrode  $\text{Pt} \left| \begin{array}{c} \text{SnCl}_2 \\ \text{alkali} \end{array} \right.$  has a high negative value, an acid solution of potassium permanganate is a powerful oxidizing agent, and an alkaline solution of stannous chloride is a strong reducing agent.

The applicability of equation 6 is demonstrated by the data given in Table LXI. These data were obtained by Peters<sup>1</sup> with the ferro-ferri

TABLE LXI  
OXIDATION POTENTIALS

Ratio $\text{Fe}^{+++} : \text{Fe}^{++}$ in Per Cent	Observed emf $E$	Absolute p.d. of the $\text{Pt} \left  \begin{array}{c} \text{Fe}^{+++} \\ \text{Fe}^{++} \end{array} \right.$ Electrode	Normal Oxidation Potential Referred to the Normal Calomel Electrode as Zero, $E_0$	Equilibrium Constant $K = \frac{[\text{Fe}_e^{++}]}{[\text{Fe}_e^{+++}]}$
0.5 : 99.5	+0.298	+0.858	+0.430	$10^{7.49}$
2.0 : 98	+0.333	+0.893	+0.430	$10^{7.49}$
10 : 90	+0.373	+0.933	+0.428	$10^{7.45}$
30 : 70	+0.408	+0.968	+0.429	$10^{7.44}$
40 : 60	+0.420	+0.980	+0.430	$10^{7.49}$
50 : 50	+0.431	+0.991	+0.431	$10^{7.50}$
80 : 20	+0.465	+1.025	+0.430	$10^{7.49}$
90 : 10	+0.480	+1.040	+0.425	$10^{7.40}$

electrode-calomel electrode cell discussed above. The values of  $E_0$  are calculated on the assumption—approximate at best—that the ratio of the concentrations of the ferric and ferrous ions is equal to the ratio of the concentrations of the respective salts. Peters' results for 10 per cent  $\text{Fe}^{+++}$  and 90 per cent  $\text{Fe}^{++}$  may be represented as follows:

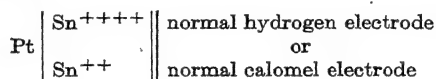


The very large value of the equilibrium constant shows that  $E$  remains positive, and ferric ions continue to be reduced, until the ratio of the concentration of the ions in the lower and higher states of oxidation is less than  $1 : 10^{-7}$ .

**Measurement of Oxidation Potentials.** In order to determine oxidation potential, a solution is prepared containing salts of the same ion but in different states of oxidation (e.g., stannous and stannic chlorides).

<sup>1</sup> *Z. physik. Chem.*, **26**, 193 (1898).

Some of the solution is placed in each of two potential vessels, and electrodes are inserted, which must not be attacked by any component taking part in the reaction. Although the potential differences of the two electrodes should be the same, they seldom are; but they attain the same value on standing. Sometimes this may necessitate days of waiting. Spencer and Abegg<sup>1</sup> showed, however, that if platinized platinum electrodes are employed, which are first polarized, either cathodically or anodically, before being inserted in the potential vessels, the potential difference is the same for each almost immediately. The electrodes may be polarized by immersing them in a dilute solution of sulphuric acid and passing a current between them for some minutes. One of the electrodes is then combined with either a normal hydrogen or calomel electrode, thus:



and the electromotive force of the combination is measured.

Since all oxidation potentials should be expressed on the basis that the tendency of hydrogen to pass from the ionic to the atomic state is zero, when in contact with a solution which is normal with respect to hydrogen ions, the electromotive force of the above combination, when measured against the normal calomel electrode, should be reduced to the hydrogen value. This value represents the oxidation potential  $E$  referred to that of hydrogen in contact with a normal solution of its ions as zero. From the value of  $E$  thus obtained, the value of the normal oxidation potential,  $E_0$ , may be calculated by means of equation 6.

The earliest work on the determination of oxidation potentials was carried out by Bancroft,<sup>2</sup> who measured the potential differences between platinized electrodes and solutions containing, in most cases, 0.2 mole of electrolyte per liter. Although these values are not accurate, they are given in Table LXII because they are measures of the oxidizing power of the substances.

Although the electromotive behavior of oxidizing agents has been studied by a number of investigators,<sup>3</sup> existing data on normal oxidation

<sup>1</sup> *Z. anorg. Chem.*, **44**, 379 (1905).

<sup>2</sup> *Z. physik. Chem.*, **10**, 387 (1892).

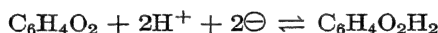
<sup>3</sup> Haber and Grinberg, *Z. anorg. Chem.*, **18**, 37 (1898); Schaum, *Z. Elektrochem.*, **5**, 316 (1899); Crotofino, *Z. anorg. Chem.*, **24**, 225 (1900); Fredenhagen, *ibid.*, **29**, 396 (1902); Spencer and Abegg, *ibid.*, **44**, 379 (1905); Sammet and Luther, *Z. Elektrochem.*, **11**, 293 (1905); Abegg and Loimaranta, *ibid.*, **13**, 33 (1907); Abegg, *ibid.*, **13**, 289 (1907); Foerster and Yamasaki, *ibid.*, **17**, 361 (1911); Kolthoff, *Chem. Weekblad*, **16**, 1406 (1919).

potentials ( $E_0$ ) are neither so numerous nor so accurate as the importance of the subject warrants. In Table LXIII are given a number of normal oxidation potentials that have been accurately determined. These values depend somewhat on the concentrations of the ions employed in determining  $E$  and, usually, markedly on the acid or alkali concentration.

TABLE LXII  
OXIDATION POTENTIALS

Substance	$H^+ \rightarrow H = 0$ $E_{(C^+ \leftarrow C')}$
Stannous chloride in potassium hydroxide	-0.578 volt
Hydroxylamine, potassium hydroxide	-0.333 volt
Pyrogallol, potassium hydroxide	-0.200 volt
Iodine, potassium hydroxide	+0.213 volt
Stannous chloride, hydrochloric acid	+0.219 volt
Cupric chloride	+0.283 volt
Sulphurous acid	+0.441 volt
Potassium ferricyanide	+0.705 volt
Potassium bichromate	+0.785 volt
Chlorine, potassium hydroxide	+0.91 volt
Ferric chloride	+0.96 volt
Nitric acid	+0.98 volt
Potassium iodate	+1.21 volts
Potassium permanganate	+1.49 volts

Since the change of quinone to hydroquinone in the quinhydrone electrode may be represented by the electrochemical equation



the oxidation potential at 25° is given by the equation

$$E_{(C_0 \leftarrow C')} = E_0 + \frac{0.059}{2} \log \frac{[\text{quinone}][H^+]^2}{[\text{hydroquinone}]} \quad (7)$$

As quinhydrone is an equimolecular compound of hydroquinone and quinone and, therefore, the concentrations of the substances are equal, equation 7 becomes

$$E_{(C_0 \leftarrow C')} = E_0 + 0.059 \log [H^+] \quad (8)$$

At 25°,  $E_0 = 0.6990$  volt (referred to the normal hydrogen electrode).<sup>1</sup> When the normal calomel electrode is employed with the quinhydrone

<sup>1</sup> Bülmann and Lund, *Ann. phys. chim.*, [ix], 16, 327 (1921).



electrode, the hydrogen-ion concentration may be calculated by means of the expression

$$-\log [\text{H}^+] = p_{\text{H}} = \frac{0.4185 - E}{0.059} \quad (9)$$

which follows directly from equation 8.

TABLE LXIII  
NORMAL OXIDATION POTENTIALS

Electrode		Temperature	$E_0$ Volts ( $\text{H}^+ \rightarrow \text{H} = 0$ )	Authority
Pt	$\text{Co}^{+++}$ $\text{Co}^{++}$	..	+1.76	Oberer <sup>1</sup>
Pt	$\text{Mn}^{++++}$ $\text{Mn}^{+++}$	+15 N $\text{H}_2\text{SO}_4$ 12°	+1.642	Grube and Huberich <sup>2</sup>
Pt	$\text{Ce}^{++++}$ $\text{Ce}^{+++}$	(acid with $\text{HNO}_3$ ) 25°	+1.6095	Noyes and Garner <sup>3</sup>
Pt	$\text{Mn}^{++++}$ $\text{Mn}^{++}$	+15 N $\text{H}_2\text{SO}_4$ 12°	+1.577	Grube and Huberich <sup>2</sup>
Pt	$\text{Mn}^{+++}$ $\text{Mn}^{++}$	+15 N $\text{H}_2\text{SO}_4$ 12°	+1.511	Grube and Huberich <sup>2</sup>
Pt	$\text{Ce}^{++++}$ $\text{Ce}^{+++}$	(sulphates, slightly acid with $\text{H}_2\text{SO}_4$ ) 17°	+1.431	Baur and Glaesson <sup>4</sup>
Pt	$\text{Ti}^{+++}$ $\text{Ti}^{+}$	(acid with $\text{HNO}_3$ ) 25°	+1.2303	Noyes and Garner <sup>5</sup>
Pt	$\text{CrO}_4^{--}$ $\text{Cr}^{+++}$	25°	+1.195	Durban and Brown <sup>6</sup>
Pt	$\text{Fe}^{+++}$ $\text{Fe}^{++}$	25°	+0.7701	Schumb and Sherrill <sup>7</sup>
Pt	$\text{Fe}(\text{CN})_6^{---}$ $\text{Fe}(\text{CN})_6^{----}$	25°	+0.406	Schaum and Linde <sup>8</sup>
Pt	$\text{Cr}^{+++}$ $\text{Cr}^{++}$	+0.1 N $\text{HCl}$ 25°	+0.400	Forbes and Richter <sup>9</sup>
Pt	$\text{Ti}^{++++}$ $\text{Ti}^{+++}$	+4 N $\text{H}_2\text{SO}_4$ 18°	+0.056	Diethelm and Foerster <sup>10</sup>
Pt	$\text{V}^{+++}$ $\text{V}^{++}$	+1 N $\text{H}_2\text{SO}_4$ 18°	-0.204	Rutter <sup>11</sup>
Hg	$\text{Sn}^{++++}$ $\text{Sn}^{++}$	+ $\text{HCl}$ 25°	-0.426 +0.011[ $\text{HCl}$ ]	Forbes and Bartlett <sup>12</sup>
Pt	$\text{Sn}^{++++}$ $\text{Sn}^{++}$	+0.6 N $\text{NaOH}$ 18°	-0.854	Foerster and Dolch <sup>13</sup>

<sup>1</sup> Dissertation, Zurich, 1903.

<sup>2</sup> *Z. Elektrochem.*, **29**, 8 (1923).

<sup>3</sup> *J. Am. Chem. Soc.*, **58**, 1265 (1936).

<sup>4</sup> *Z. Elektrochem.*, **9**, 534 (1903).

<sup>5</sup> *J. Am. Chem. Soc.*, **58**, 1268 (1936).

<sup>6</sup> *J. Phys. Chem.*, **43**, 491 (1939).

<sup>7</sup> *J. Am. Chem. Soc.*, **59**, 2360 (1937).

<sup>8</sup> *Z. Elektrochem.*, **9**, 406 (1903).

<sup>9</sup> *J. Am. Chem. Soc.*, **39**, 1140 (1917).

<sup>10</sup> *Z. physik. Chem.*, **62**, 129 (1908).

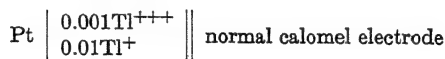
<sup>11</sup> *Z. anorg. Chem.*, **52**, 368 (1907).

<sup>12</sup> *J. Am. Chem. Soc.*, **36**, 2030 (1914).

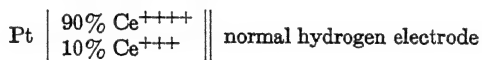
<sup>13</sup> *Z. Elektrochem.*, **16**, 599 (1910).

## PROBLEMS

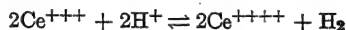
1. From data given in Table LXIII, calculate the electromotive force of the cell



2. The electromotive force of the cell



is +1.464 volts at 18°. Calculate the value of the equilibrium constant of the reaction



## CHAPTER XI

### POLARIZATION AND ELECTROLYSIS

**Polarization.** If smooth platinum electrodes are dipped in a solution of sulphuric acid, and are connected through a galvanometer with a battery having an electromotive force of less than 1.70 volts, it will be found that, although a current flows through the circuit at first, its strength, as shown by the galvanometer, rapidly decreases and at the end of a very short time becomes zero. Then, if the battery is removed and the circuit completed through a wire, it will be observed that the galvanometer is deflected in the opposite direction. By developing an electromotive force which acts in a direction opposed to that of the battery, platinum electrodes immersed in a solution of sulphuric acid possess not only the power to stop the passage of the current from a battery having an electromotive force of less than 1.70 volts, but also the ability to send a current in the opposite direction through the circuit for some time after the removal of the battery. At the instant the battery is removed from the circuit, it is found that the opposed electromotive force of the platinum electrodes is equal to about 1.70 volts. The phenomenon which has just been described is known as **polarization**, and the electrodes are said to be **polarized**.

In the example just considered, the occurrence of polarization is due to the fact that the gases formed at the electrodes are not set free entirely, a certain quantity being absorbed by the electrodes. This causes the platinum electrodes to act as gas electrodes and to develop an electromotive force which opposes that of the battery. As the gases accumulate, the opposed electromotive force gradually becomes larger and larger and, when the electromotive force of the battery is less than 1.70 volts, ultimately exceeds that of the battery, thus causing the current from it to cease. On the removal of the battery from the circuit, the platinum electrodes and the solution of sulphuric acid constitute a gas cell which, on connecting the electrodes, produces a current in the opposite direction.

Evidently, an electromotive force of 1.70 volts is required to electrolyze sulphuric acid between smooth, platinum electrodes. Since it has been found that water may be decomposed between platinized platinum electrodes with an electromotive force of 1.23 volts (the theoretical value

of the emf of the hydrogen-oxygen cell), it is probable that this value corresponds to the work required to discharge the ions at the electrodes; the difference between this value and 1.70 volts, after deducting the amount of the applied electromotive force used to overcome the ohmic resistance of the circuit, represents the additional pressure necessary to separate the liberated gases from smooth, platinum electrodes. This additional voltage, the difference between the actual observed voltage and the theoretical voltage, is termed the **polarization voltage**.

Polarization phenomena are also observed in cells in which the products of electrolysis are metallic. Thus, when smooth platinum electrodes are immersed in a solution of copper sulphate and connected to a battery having an electromotive force of less than 1.50 volts, the current which flows through the circuit soon diminishes to zero. The copper deposited on the one platinum electrode and the oxygen absorbed by the other constitute a voltaic cell, the electromotive force of which acts in a direction opposed to that of the battery. Similar phenomena have been observed in cells containing fused electrolytes, and the variation of polarization with time has been studied.<sup>1</sup>

Polarization also occurs when a solution of an electrolyte is electrolyzed between electrodes of the metal of the electrolyte. Thus, when a current is passed between silver electrodes immersed in a solution of silver nitrate, the electromotive force required exceeds that necessary to overcome the ohmic resistance of the solution. This is due to an increase in the concentration of the electrolyte about the anode and a decrease in its concentration in the neighborhood of the cathode. This results in the formation of a concentration cell, the electromotive force of which is opposed to the external electromotive force maintaining the current through the solution. Polarization due to this cause is called **concentration polarization**. Obviously, it can be diminished by vigorously stirring the solution. Concentration polarization has been observed during the electrolysis of fused salts.<sup>2</sup>

Although in the cell just considered the mechanism of polarization is obvious, in others it is obscure. Credit is due to LeBlanc<sup>3</sup> for the first attempts to disentangle polarization phenomena. He showed that polarization potentials depend upon the same principles as the potential differences in voltaic cells. Lewis and Jackson<sup>4</sup> attributed polarization "*to a counter electromotive force caused either by exhaustion of the sub-*

<sup>1</sup> Drossbach, *Z. Elektrochem.*, **43**, 891 (1937).

<sup>2</sup> Karpatshev and Rempel, *J. Phys. Chem. Russ.*, **8**, 134 (1936); cf. also Pletenev and Rozov, *ibid.*, **11**, 641 (1938).

<sup>3</sup> *Z. physik. Chem.*, **8**, 299 (1891); **12**, 333 (1893).

<sup>4</sup> *Proc. Am. Acad. Arts Sci.*, **41**, 399 (1906).

*stances used in the electrolytic reaction faster than they can be replaced, or by the accumulation of the products of this reaction faster than they can be removed.*" Since the effect of either of these factors is to increase the potential of an electrode above its equilibrium value, the polarization of an electrode may be defined as the difference between the actual and the equilibrium values of its potential. Evidently, **polarizable electrodes** are those which attain their equilibrium potential slowly. On the other hand, since electrochemical processes between metals and their ions proceed at high velocities, electrodes of these substances usually reach their equilibrium potential rapidly. Consequently, such electrodes are **unpolarizable** or only slightly polarizable.

Smits<sup>1</sup> explained cathodic and anodic polarization of metals on the assumption of a disturbance of the inner equilibrium of the metal and the slow re-establishment of this equilibrium. The rate at which the internal equilibrium is attained is markedly affected by catalysts.

The effect of polarization is to increase the electromotive force required to maintain a current through an electrolysis cell, and therefore the energy consumed in the process. From a practical standpoint it is important to be able to reduce polarization. This may often be accomplished by the addition to the cell of substances which accelerate slow electrode processes. Substances which achieve this end are called **depolarizers**. The polarization of a cathode at which hydrogen is being evolved may be diminished by the addition of some substance which will react with the hydrogen<sup>2</sup> (see the following chapter). In the electrolysis of silver nitrate, discussed above, **depolarization** is brought about by vigorous stirring.

**Passivity.** It is well known that a piece of iron with a fresh metallic surface does not dissolve on being dipped into concentrated nitric acid. Neither does copper deposit on the iron when it is removed from the acid, washed, and immersed in a solution of copper sulphate. This behavior, known as **passivity**, was first observed with iron at the end of the eighteenth century.<sup>3</sup> Later the phenomenon was found to occur with chromium, nickel, and other metals.

Many base metals become passive when made the anode in an electrolytic cell. In this state the metals behave like noble metals and either do not enter solution at all or do not dissolve in accordance with Faraday's law. Thus chromium and manganese dissolve, when passive, with a higher valence than when active. This electrochemical passivity, which is analogous to chemical passivity, is intimately related to polari-

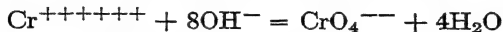
<sup>1</sup> *The Theory of Allotropy*, pp. 130-33, 1922; *Trans. Faraday Soc.*, **19**, 772 (1924).

<sup>2</sup> Cf. Haber, *Z. physik. Chem.*, **32**, 193 (1900).

<sup>3</sup> Cf. Keir, *Phil. Trans.*, **80**, 359 (1790).

zation. Indeed, passivity may ultimately turn out to be pure polarization.

The phenomenon of passivity is of interest to the electrochemist. In order to cause a passive anode to dissolve, a higher anodic polarization is necessary than would be required otherwise, and sometimes this excess polarization will cause another electrode process to take place. For example, Hittorf<sup>1</sup> showed that in alkaline solution a passive chromium anode does not enter solution until the potential reaches about +0.34 volt. Then it dissolves as  $\text{Cr}^{++++++}$  ions, which immediately react with the hydroxyl ions present to form chromate ions



The passivity of metals has engaged the attention of chemists for many years, and numerous explanations, both physical and chemical, have been put forward to account for the phenomenon. Indeed, few subjects have given rise to such differences of opinion. At least three explanations have enjoyed favor at different times: (1) the oxide theory of Faraday;<sup>2</sup> (2) the theory of modifications with different valences;<sup>3</sup> (3) LeBlanc's theory of reaction velocity.<sup>4</sup> According to LeBlanc's theory, a metal is passive if the velocity of the change to the ionic state is slow, and *vice versa*. These and many other theories have been critically reviewed by Bennett and Burnham,<sup>5</sup> who find them all either inadequate or untenable. According to these investigators, passivity is invariably due to the formation of an oxide which is adsorbed by the metal forming a surface film.<sup>6</sup> This film, being more noble than the metal, protects it from the action of the solution. Thus oxidizing conditions promote passivity, and reducing conditions develop activity. It has been found that the formation of anodic films on aluminum and the passivity of nickel anodes in acid solution are promoted by the action of ultrasonic waves, whereas the passivity of iron and chromium in nitric acid is destroyed by this agency.<sup>7</sup>

**Decomposition Voltage.** From what has been said under polarization, it is clear that a continuous current will flow between smooth platinum electrodes immersed in sulphuric acid only when the external electromotive force exceeds the back electromotive force of the electrodes. The

<sup>1</sup> *Z. Elektrochem.*, **4**, 482 (1898); **6**, 6 (1899); **7**, 168 (1900).

<sup>2</sup> *Phil. Mag.*, **9**, 122 (1836).

<sup>3</sup> Finkelstein, *Z. physik. Chem.*, **39**, 91 (1901).

<sup>4</sup> *Z. Elektrochem.*, **6**, 472 (1900); **11**, 8, 705 (1905); *Boltzmann Festschrift*, 1904, 183; *Trans. Faraday Soc.*, **9**, 251 (1914).

<sup>5</sup> *Trans. Am. Electrochem. Soc.*, **29**, 217 (1916).

<sup>6</sup> Cf. also Lepin, *Acta Physicochim. U.R.S.S.*, **8**, 659 (1938).

<sup>7</sup> Schmid and Ehret, *Z. Elektrochem.*, **43**, 408 (1937).

smallest external electromotive force that must be applied, in order to bring about the separation of such quantities of cations and anions at insoluble electrodes that a continuous current flows through the solution, is called the **decomposition voltage** of the electrolyte. As the back electromotive force of the cell is equal to the algebraic difference of the potential differences which exist at the electrode-solution junctions, it follows

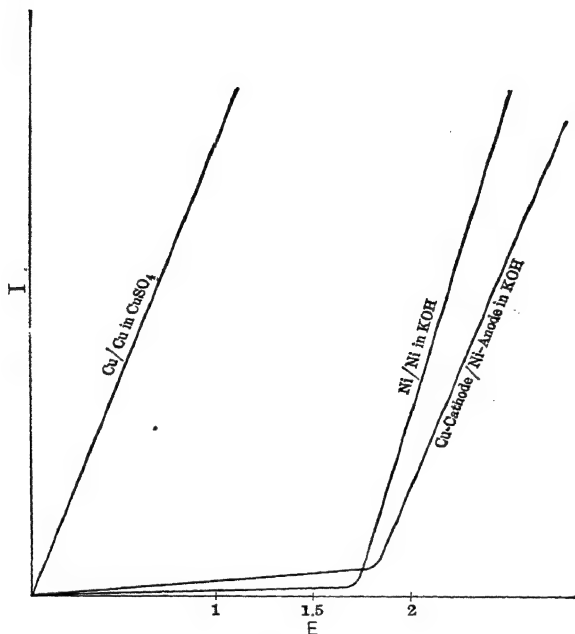


FIG. 71.

that the decomposition voltage of an electrolyte is the difference of the potentials required to separate the anion and cation, respectively, and that it must just exceed the difference of the electrode potentials. Consequently, for a solution of an electrolyte of molal ion concentration, the decomposition voltage must be slightly greater than the difference of the electrolytic potentials of the cation and anion, respectively (see Table LIV), *provided that the electrodes are not polarized*.

**The Measurement of Decomposition Voltage.** The decomposition voltage of an electrolyte may be determined, approximately, by allowing electrolysis to proceed for some time with an electromotive force which is greater than the back electromotive force of the cell. The circuit is

then broken and the back electromotive force measured immediately by means of a well-damped voltmeter of high resistance. The voltmeter reading represents the decomposition voltage of the electrolyte. A second method consists in gradually increasing the external electromotive force applied to the electrodes and noting the voltage at which a sudden

TABLE LXIV  
DECOMPOSITION VOLTAGES

Electrolyte	Decomposition Voltage, volts
Zinc sulphate	2.55
Zinc bromide	1.80
Nickel sulphate	2.09
Nickel chloride	1.85
Lead nitrate	1.52
Cadmium sulphate	2.03
Cadmium nitrate	1.98
Cobalt sulphate	1.92
Cobalt chloride	1.78
Copper sulphate	1.49
Silver sulphate	0.80
Silver nitrate	0.70
Sodium hydroxide	1.69
Potassium hydroxide	1.67
Ammonium hydroxide	1.74
Sulphuric acid	1.67
Nitric acid	1.69
Phosphoric acid	1.70
Monochloroacetic acid	1.72
Dichloroacetic acid	1.66
Perchloric acid	1.65
Acetic acid	1.57
Trichloroacetic acid	1.51
Hydrochloric acid	1.31
Azoic acid	1.29
Oxalic acid	0.95
Hydrobromic acid	0.94
Hydriodic acid	0.52

increase in the current takes place, this increase being indicated by a milliammeter contained in the circuit. If the voltage  $E$  is plotted against the current strength  $I$ , as shown in Fig. 71, the point of discontinuity on the curve corresponds to the decomposition voltage. The uncertainties attached to decomposition voltages determined by this method can be removed, to some extent, by the use of rotating electrodes.<sup>1</sup>

<sup>1</sup> Cf. Bennowitz, *Z. physik. Chem.*, **72**, 220 (1910).



In Table LXIV are given the decomposition voltages of molal solutions of various electrolytes between platinum electrodes,<sup>1</sup> and in Table LXV values for a number of molten electrolytes.<sup>2</sup>

TABLE LXV  
DECOMPOSITION VOLTAGES OF MOLTEN ELECTROLYTES

Electrolyte	Temperature, °C	Decomposition Voltage, volts
Sodium fluoride	920	2.80
Potassium fluoride	860	2.01
Lithium chloride	800	3.16
Sodium chloride	810	3.24
Potassium chloride	800	3.34
Sodium bromide	800	2.75
Potassium bromide	800	2.88
Sodium iodide	800	2.22
Potassium iodide	800	2.405
Magnesium chloride	800	2.49
Barium chloride	1005	3.14
Calcium chloride	800	3.21
Zinc chloride	400	1.96
Sodium hydroxide	200	2.32
Sodium hydroxide	300	2.25
Potassium hydroxide	260	2.4
Potassium hydroxide	300	2.35

Very often it is not practical or convenient to measure the decomposition voltage; under these circumstances the value may be determined theoretically with the aid of the Gibbs-Helmholtz equation (equation 12a, Chapter VIII).

**Overvoltage.** The decomposition voltage of an electrolyte varies with the nature of the electrodes between which the solution is electrolyzed. Thus, a higher voltage is required to decompose a solution of sulphuric acid between a platinum anode and a lead cathode than between two platinum electrodes. This arises from the fact that more work must be expended to liberate hydrogen from a lead than from a platinum cathode. The variation in decomposition voltage with the electrode material results from differences in polarization. The differ-

<sup>1</sup> LeBlanc, *Z. physik. Chem.*, **8**, 299 (1891).

<sup>2</sup> Neumann and Bergve, *Z. Elektrochem.*, **21**, 143 (1915); Moltschanov, *Legkie Metal.*, **4**, 28 (1935); Kirk and Bradt, *Trans. Electrochem. Soc.*, **70**, 244 (1936); Tverovski and Moltschanov, *J. Phys. Chem. Russ.*, **9**, 239 (1937); Grothe and Savelsberg, *Z. Elektrochem.*, **46**, 336 (1940). The difficulties encountered in the determination of the decomposition voltage of molten electrolytes are discussed by Drossbach, *Trans. Electrochem. Soc.*, **70**, 249 (1936).

ence between the electrode potential required for the passage of the current and its equilibrium value is called the **overvoltage** of the electrode. It is an electromotive force which acts counter to the applied electromotive force during electrolysis and represents the excess of energy required to form a substance over that given by the resolution of the product formed to the original state.<sup>1</sup> Thus the hydrogen overvoltage of an electrode is the difference between its potential when hydrogen is liberated during electrolysis and the potential of the reversible hydrogen electrode, both potentials being referred to the same electrolyte. Overvoltage varies with the nature of the electrode process. Although considerations of overvoltage are usually limited to hydrogen and oxygen, other gases and the metals also have definite overvoltages.

For a long time the whole subject of overvoltage, its magnitude, properties, and determining factors, remained in a confused state, notwithstanding the practical importance of overvoltage effects in electrolytic processes. Indeed, it was well known that electrolytic methods of oxidation and reduction were often attended with uncertainty as to yield and current efficiency, owing to variations in the overvoltages of the electrodes. Although a great many measurements<sup>2</sup> of overvoltage had been made, including those by Caspari<sup>3</sup> of the overvoltage required with different metals for the separation of hydrogen, and similar determinations by Coehn and Osaka<sup>4</sup> for oxygen, it was not until three decades ago that the subject was first extensively and systematically studied, by Newbery,<sup>5</sup> with the object of furnishing data that might be employed in producing and maintaining definite overvoltages in electrolytic processes. In this investigation several thousand determinations on twenty different materials were made. The results obtained with different metals in acid and alkaline solutions show, in general, that oxygen overvoltages are much higher than the corresponding effects for hydrogen. It is due to this that electrolytic oxidation of organic compounds tends to yield highly oxidized products (ultimately carbon dioxide), whereas corresponding reduction processes can be more

<sup>1</sup> Bennett and Thompson, *J. Phys. Chem.*, **20**, 296 (1916).

<sup>2</sup> Cf. Kaufler, *Z. Elektrochem.*, **13**, 635 (1907); **14**, 321, 737, 749 (1908); Müller, *ibid.*, **13**, 681 (1907); Nutton and Law, *Trans. Faraday Soc.*, **3**, 50 (1907); Möller, *Drudes Ann.*, **25**, 725 (1908); *Z. physik. Chem.*, **65**, 226 (1909); Sacerdoti, *Z. Elektrochem.*, **17**, 473 (1911); Pring and Curzon, *Trans. Faraday Soc.*, **7**, 237 (1912); Pring, *Z. Elektrochem.*, **19**, 255 (1913); Thiel and Bruening, *Z. anorg. Chem.*, **83**, 329 (1913); Crabtree, *Trans. Faraday Soc.*, **9**, 125 (1913); Richards, *ibid.*, **9**, 140 (1913).

<sup>3</sup> *Z. physik. Chem.*, **30**, 89 (1899).

<sup>4</sup> *Z. anorg. Chem.*, **34**, 86 (1903).

<sup>5</sup> *J. Chem. Soc.*, **105**, 2420 (1914); **109**, 1051, 1066 (1916); *Mem. Proc. Manchester Lit. Phil. Soc.*, **61**, No. 9 (1916).

readily graded. The results of Newbery's investigation also show that the magnitude of the hydrogen overvoltage of a metal is determined by its position in the periodic table, the overvoltage increasing to group II and thereafter decreasing gradually to group VIII, as is shown by Table LXVI.

TABLE LXVI  
HYDROGEN OVERVOLTAGE OF METALS AND THEIR POSITION IN THE PERIODIC TABLE

Group in the Periodic Table	Metal	Typical Overvoltage
I	Na, Cu, Ag, Au	0.35 volt
II	Mg, Zn, Cd, Hg	0.70 volt
III	Al, Ti	0.50 volt
IV	C, Sn, Pb	0.45 volt
V	Sb, Ta, Bi	0.42 volt
VI	Cr, Mo, W	0.32 volt
VII	Mn	0.25 volt
VIII	Fe, Ni, Rh, Pt, Ir	0.18 volt

In acid solution the hydrogen overvoltage of a metal increases as its melting point decreases.<sup>1</sup> Thus, mercury, with the lowest melting point of the metals, has the highest of all hydrogen overvoltages; and rhodium, with a melting point above 3000°, has the lowest hydrogen overvoltage. No change in the hydrogen overvoltage of gallium or Wood's metal occurs on melting or freezing.<sup>2</sup> This behavior indicates that the hydrogen overvoltage of these metals is independent of their internal structure.

The hydrogen overvoltage of binary alloys was studied by Fischer,<sup>3</sup> who found that it is independent of the proportions of the metals but depends on the component which in the pure state has the lower overvoltage.

The following results were obtained by Newbery for a number of metals and carbon:

#### HYDROGEN OVERVOLTAGE

*Gold:* In acid electrolytes the overvoltage rises rapidly at first, but falls to a much lower value after repeated subjection to high current densities.

*Platinum:* In acid solution with a high current density the overvoltage exceeds 0.5 volt in twenty-four hours.

<sup>1</sup> Weeks, *Chem. News*, **129**, 17 (1924).

<sup>2</sup> Butts and Johnson, *Trans. Electrochem. Soc.*, **70**, 259 (1936).

<sup>3</sup> *Z. physik. Chem.*, **113**, 326 (1924).

*Copper:* With alkaline electrolytes the overvoltage is higher than with acid electrolytes; but traces of impurities lower the overvoltage of this metal.

*Silver:* The overvoltage is more constant than that of copper and less susceptible to slight impurities. Cathodes of copper or nickel with a fairly thick, rough electrolytic deposit of silver (from a cyanide bath) are useful for moderate reductions.

*Lead, Zinc, and Tin:* Very high overvoltages are attainable with these metals. The overvoltage of zinc is more stable at high current densities than that of lead. Traces of impurities, notably platinum, render a lead or tin cathode useless for powerful reductions.

*Nickel:* The overvoltage of this metal in alkaline electrolytes is fairly constant, but it varies considerably in acid solution.

*Mercury and Amalgams:* Mercury has a high overvoltage. Amalgamation increases the overvoltage of all metals. Amalgamated zinc and lead cathodes are very stable, and these electrodes appear to be ideal for the most powerful reductions.

*Carbon:* At low current densities the overvoltages of gas carbon and graphite are nearly the same, but at higher current densities the overvoltage of the gas carbon is decidedly greater, especially in acid electrolytes.

*Iron:* Alloys of iron which require high current densities to produce their maximum overvoltage are likely to offer a high resistance to corrosion. Tantiron or chromiron cathodes are recommended for highly efficient reductions in acid solutions.

## OXYGEN OVERVOLTAGE

*Gold:* This metal has a high overvoltage but suffers badly from disintegration. The overvoltage in acid solution is steady, its maximum value being reached at about 4 milliamperes per square centimeter. In alkaline solution the overvoltage is higher, its maximum occurring at 400 milliamperes per square centimeter.

*Platinum:* This is the only readily available metal capable of withstanding the action of the nitrate and sulphate ions in concentrated acids. In both acids and alkalis the overvoltage is the same: 0.86 volt up to 20 milliamperes per square centimeter, but between 20 and 50 milliamperes it rises suddenly to 0.99 volt.

*Copper:* This metal shows no sign of passivity in acid solutions, but the passive state is readily produced in alkaline solution. Copper is a very suitable anode material for moderate oxidations, but it cannot be used for a long period as it is slowly attacked and deposited on the cathode.

*Lead:* This metal is a suitable material for anodes in oxidation reactions in dilute sulphuric acid solutions. Unlike other metals it becomes passive more readily in acid than in alkaline solutions.

*Nickel and Cobalt:* In alkaline solution pure nickel anodes become passive at even the lowest current densities; with nickel anodes containing a small percentage of copper passivity is only partial. Nickel anodes also become passive in dilute sulphuric acid. Unlike nickel, cobalt anodes do not become passive in dilute sulphuric acid. Even at a current density of 2000 milliamperes per square centimeter they are still active. In alkaline solution anodes of this metal instantly become passive and an overvoltage of 0.57 volt is obtained.

*Iron and tantiron* readily become passive at low current densities when anode. The overvoltage of tantiron is somewhat higher than that of iron, but electrodes of each material have a correspondingly higher overvoltage in acid (0.88 and 0.75 volt) than in alkaline (0.54 and 0.49 volt) solution.

*Tin:* This metal when anode shows no passivity in acid solution but readily becomes passive in alkaline solution; the overvoltage rises to a high value in alkaline solution but it is very erratic.

*Carbon:* Both graphite and gas carbon disintegrate readily in acid and slightly in alkaline solution. The overvoltage of graphite rises rapidly with current density.

*Aluminum:* Anodes of aluminum become passive in alkaline solution at a current density of 600 milliamperes per square centimeter, giving an overvoltage of 0.95 volt. When the current density is reduced to 400 milliamperes, the overvoltage drops to 0.01 volt.

*Iridium* has an exceptionally low overvoltage, which remains very constant at all current densities.

TABLE LXVII

## "METAL" OVERVOLTAGES

Metal	Cathode Overvoltage, volt	Anode Overvoltage, volt
Silver	0.00	....
Lead	0.00	....
Cadmium	0.01	0.01
Zinc	0.02	0.01
Copper	0.02	0.02
Thallium	0.02	1.68
Iron	0.30	1.88
Cobalt	0.46	0.05
Nickel	0.82	1.75

In Table LXVII are given cathodic and anodic "metal" overvoltages in the respective metal sulphate solutions at a current density of 0.1 ampere per square centimeter, as determined by Newbery. With the exception of iron, nickel, and cobalt, the cathode overvoltages are very small. Overvoltages of hydrogen and oxygen will be found in the five following tables.

**The Influence of Current Density on Overvoltage.** Notwithstanding the great technical importance of this phase of overvoltage, prior to Newbery's investigations only isolated values or values over but a small range of relatively low current densities had been measured. Newbery's determinations of overvoltage were carried out over a range of current density of 0.01 to 10 amperes per square centimeter. Knobel, Caplan, and Eiseman<sup>1</sup> also studied the effect of current density on overvoltage, using a method different from that employed by Newbery. In this investigation, the hydrogen, oxygen, and halogen overvoltages of carbon and a large number of metals and alloys were determined. The hydrogen overvoltages were measured in 2 *N* sulphuric acid solution, the oxygen overvoltages in normal potassium hydroxide solution, and the overvoltages of the halogens in saturated solutions of the sodium or potassium halide, saturated further with the pure halogen. The results of this investigation are given in Tables LXVIII to LXXII. It will be observed that the hydrogen overvoltage of metals of "high overvoltage," such as mercury, lead, and cadmium, increases rapidly at first at low current densities and then but slightly with increasing current density; that of metals of "low overvoltage," such as copper and gold, increases more gradually with the current density but may finally attain as high a value as the overvoltage of the "high overvoltage" metals. Platinized platinum holds a unique position, in that it maintains its low hydrogen overvoltage even at high current densities.

On the assumption that the current strength is proportional to the rate at which atomic hydrogen is removed in the form of molecules, the relation between the cathodic overvoltage  $E$  and the current density  $I$  is usually expressed by the equation

$$E = a + b \ln I \quad (1)$$

where  $a$  and  $b$  are constants.<sup>2</sup> Overvoltage data for a number of cathode materials, such as bismuth, iron, nickel, tungsten, and platinized platinum, are in excellent agreement with this equation up to current densities of 1 ampere per square centimeter; but cathodes of mercury, copper,

<sup>1</sup> *Trans. Am. Electrochem. Soc.*, **43**, 55 (1923).

<sup>2</sup> Tafel, *Z. physik. Chem.*, **50**, 641 (1905); cf. Westrip, *J. Chem. Soc.*, **125**, 1112 (1924).

TABLE LXVIII

HYDROGEN OVERVOLTAGES AT 25° C

Current Density milliamperes per sq cm	Overvoltages in Volts													
	Au	Cd	Cu	Plat- inized Pt	Smooth Pt	Al	Graph- ite	Ag	Sn	Fe	Chem- metal	Brass	Monel Metal	Dur- iron
0	....	0.466	....	0.000	....	....	0.0022	....	0.2411	0.2026	0.2824	....	....	0.1680
0.1	0.122	0.651	0.351	0.0034	....	0.499	0.3166	0.2981	0.3995	0.2183	0.3160	0.3832	0.1911	0.1710
1	0.241	0.981	0.479	0.0154	0.024	0.565	0.5995	0.4751	0.8561	0.4036	0.6592	0.4967	0.2754	0.1970
2	....	....	....	0.0208	0.034	0.625	0.6520	0.5787	0.9469	0.4474	0.7249	0.5346	0.3022	0.2136
5	0.332	1.086	0.548	0.0272	0.051	0.745	0.7250	0.6922	1.0258	0.5024	0.7885	0.5960	0.3387	0.2443
10	0.390	1.134	0.584	0.0300	0.068	0.826	0.7788	0.7618	1.0767	0.5571	0.8349	0.6459	0.3832	0.2856
50	0.507	1.211	....	0.0376	0.186	0.968	0.9032	0.8300	1.1851	0.7000	0.9322	0.8011	0.5345	0.5096
100	0.588	1.216	0.801	0.0405	0.288	0.996	0.9774	0.8749	1.2230	0.8184	0.9696	0.9104	0.6244	0.6129
200	0.668	1.228	0.988	0.0420	0.355	1.176	1.0794	0.9379	1.2342	0.9854	0.9989	1.1088	0.7108	0.7240
500	0.770	1.246	1.186	0.0448	0.573	1.237	1.1710	1.0300	1.2380	1.2561	1.0407	1.2318	0.8619	0.8591
1000	0.798	1.254	1.254	0.0483	0.676	1.286	1.2200	1.0890	1.2306	1.2915	1.0682	1.2544	1.0716	1.0205
1500	0.807	1.257	1.269	0.0495	0.768	1.292	1.2208	1.0841	1.2286	1.2908	1.0859	1.2491	1.2095	1.1400

TABLE LXVIII—Continued

HYDROGEN OVERVOLTAGES AT 25° C

Overvoltages in Volts											
Current Density milliamperes per sq cm	Zn	Carbon	Bi	Ni	Pb	Current Density	Overvoltage Hg	Current Density	Overvoltage Te	Current Density	Overvoltage Pd
	0.716	....	0.78	0.563	0.52	0.00	0.2805	0.000	.....	0.000	.....
	0.726	....	....	0.633	.....	0.0769	0.5562	0.416	0.0504	0.227	0.0546
	0.726	0.64	0.98	0.705	1.060	0.769	0.8488	0.832	0.3505	1.135	0.1392
	0.746	0.70	1.05	0.747	1.090	1.54	0.9295	1.667	0.4162	2.27	0.1820
	0.926	0.82	1.15	0.890	1.168	3.87	1.0060	4.16	0.4405	4.54	0.2349
	1.064	0.89	1.14	1.048	1.179	7.69	1.0361	8.32	0.1530	11.35	0.3165
	1.168	1.04	1.20	1.130	1.217	38.7	1.0634	41.6	0.4705	22.7	0.4034
	1.201	1.10	1.21	1.208	1.235	76.9	1.0665	83.2	0.4733	113.5	0.7205
	1.229	1.17	1.23	1.241	1.262	154	1.0751	166.7	0.4986	227	0.8607
	1.243	1.23	1.29	1.254	1.290	387	1.1053	416	0.5370	454	0.9521
	....	....	....	....	....	769	1.108	832	0.5940	1135	1.0513
	....	....	....	....	....	1153	1.126	1250	0.6590	2270	1.1168
....	....	....	....	....	.....	.....	.....	.....	.....	3400	1.1570



TABLE LXIX  
CHLORINE OVERVOLTAGES AT 25° C

Platinized Platinum		Smooth Platinum		Graphite	
Current Density milliamperes per sq cm	Over- voltage	Current Density milliamperes per sq cm	Over- voltage	Current Density milliamperes per sq cm	Over- voltage
1.1	0.0060	1.1	0.008	40	0.186
5.7	0.0140	5.7	0.0199	70	0.193
14.5	0.0180	11.4	0.0299	100	0.251
21.7	0.0190	22.8	0.0378	200	0.298
38.8	0.0210	43.0	0.0457	500	0.417
60	0.024	100	0.0540	740	0.466
100	0.026	200	0.0870	980	0.489
200	0.035	500	0.161	1131	0.535
520	0.050	750	0.212	....	....
1340	0.089	1000	0.236	....	....
1490	0.103	1350	0.263	....	....

TABLE LXX  
BROMINE OVERVOLTAGES AT 25° C

Platinized Platinum		Smooth Platinum		Graphite	
Current Density milliamperes per sq cm	Over- voltage	Current Density milliamperes per sq cm	Over- voltage	Current Density milliamperes per sq cm	Over- voltage
10	0.002	20	0.002	10	0.002
30	0.005	30	0.004	30	0.008
50	0.007	50	0.006	50	0.016
100	0.012	230	0.033	100	0.27
200	0.025	300	0.057	200	0.54
300	0.041	360	0.113	300	0.81
420	0.056	400	0.156	390	0.108
500	0.069	420	0.164	550	0.163
590	0.082	440	0.178	740	0.218
760	0.130	520	0.266	840	0.253
940	0.202	720	0.379	990	0.329
...	....	...	....	1110	0.356
...	....	...	....	1210	0.400

TABLE LXXI  
IODINE OVERVOLTAGES AT 25° C

Platinized Platinum		Smooth Platinum		Graphite	
Current Density milliamperes per sq cm	Over- voltage	Current Density milliamperes per sq cm	Over- voltage	Current Density milliamperes per sq cm	Over- voltage
10	0.006	12.3	0.0039	1.2	0.002
20	0.012	23	0.0070	5.7	0.007
40	0.022	50	0.0127	11.7	0.0139
110	0.032	90	0.0216	19.7	0.0239
220	0.050	130	0.0353	34.8	0.0348
400	0.070	200	0.0510	50	0.0538
710	0.118	310	0.0744	100	0.0974
810	0.130	520	0.120	200	0.175
1000	0.196	690	0.150	400	0.315
1300	0.216	1030	0.220	590	0.451
1460	0.266	1160	0.245	840	0.645
....	.....	1330	0.277	...	.....
....	.....	1500	0.292	...	.....

TABLE LXXII  
OXYGEN OVERVOLTAGES AT 25° C

Current Density milli- amperes per sq cm	Overvoltage in Volts								
	Soft Graph- ite	Au	Cu	Ag	Chem- metal	Smooth Pt	Plat'z'd Pt	Smooth Ni	Spongy Ni
1	0.525	0.673	0.422	0.580	0.55	0.721	0.398	0.353	0.414
5	0.705	0.927	0.546	0.674	0.90	0.80	0.480	0.461	0.511
10	0.896	0.963	0.580	0.729	1.02	0.85	0.521	0.519	0.563
20	0.963	0.996	0.605	0.813	.....	0.92	0.561	.....	.....
50	.....	1.064	0.637	0.912	1.10	1.16	0.605	0.670	0.653
100	1.091	1.244	0.660	0.984	1.084	1.28	0.638	0.726	0.687
200	1.142	.....	0.687	1.038	1.101	1.34	.....	0.775	0.714
500	1.186	1.527	0.735	1.080	1.127	1.43	0.705	0.821	0.740
1000	1.240	1.63	0.793	1.131	1.154	1.49	0.766	0.853	0.762
1500	1.282	1.68	0.836	1.14	1.175	1.38	0.786	0.871	0.759

carbon, cadmium, tin, aluminum, platinum, rhodium, and lead all show deviations, there being a tendency for the overvoltage to become constant at high current densities.<sup>1</sup> The hydrogen overvoltage of silver and of silver amalgam, in 5 *N* hydrochloric and sulphuric acid, is still a

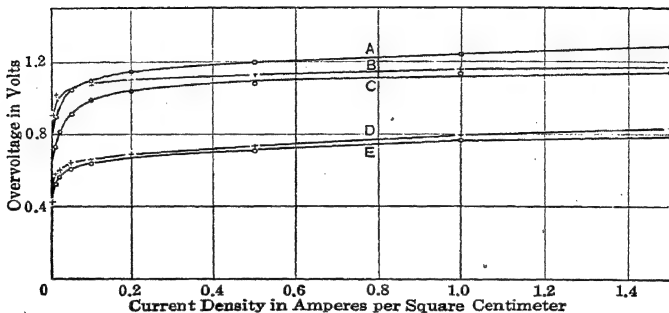


FIG. 72.

linear function of the current density up to 100 amperes per square centimeter.<sup>2</sup> Equation 1 also expresses the hydrogen overvoltage of mercury in aqueous<sup>3</sup> and ethyl alcohol<sup>4</sup> solutions of hydrogen chloride, and of nickel in liquid ammonia at  $-50^{\circ}$ .<sup>5</sup>

The current density-overvoltage curve (Fig. 72) is logarithmic in form, but seldom can the entire portion of the curve be expressed by a simple logarithmic equation. The curves in Fig. 72 show the change with current density in the oxygen overvoltage of graphite (A), chem-metal (B), silver (C), copper (D), and platinized platinum (E).

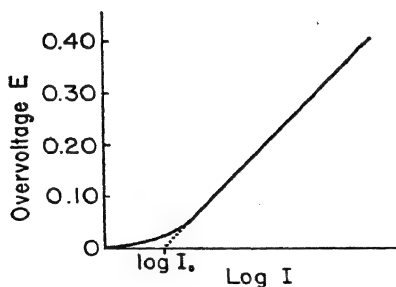


FIG. 73.

Tafel pointed out that the constant  $b$  in equation 1 was approximately equal to one-half the well-known factor,  $RT/F$ . Hence, on writing  $b = RT/\alpha F$ , we may put equation 1 in the form

$$E = 2.303 \frac{RT}{\alpha F} (\log I - \log I_0) \quad (2)$$

<sup>1</sup> Hickling and Salt, *Trans. Faraday Soc.*, **36**, 1226 (1940).

<sup>2</sup> Kabanov, *J. Phys. Chem. Russ.*, **8**, 486 (1936).

<sup>3</sup> Naray-Szabo, *Naturwiss.*, **25**, 12 (1937).

<sup>4</sup> Levina and Silberfarb, *Acta Physicochim. U.R.S.S.*, **4**, 275 (1936).

<sup>5</sup> Pleskov, *ibid.*, **11**, 305 (1939).

By plotting experimental observations (Fig. 73) and extrapolating the straight-line portion of the curve to  $E = 0$  (i.e., to the reversible hydrogen potential of the solution), the intercept gives the value of  $I_0$ . Values of  $I_0$  and  $\alpha$  for a number of materials are shown in Table LXXIII.<sup>1</sup>

TABLE LXXIII  
FACTORS FOR CALCULATING HYDROGEN OVERVOLTAGES

Cathode Material	Solution	Temperature	$\alpha$	$I_0$ amperes per sq cm
Mercury	0.1 N HCl	25°	0.49	$1.7 \times 10^{-12}$
	0.2 N H <sub>2</sub> SO <sub>4</sub>	25	0.52	$6 \times 10^{-12}$
	0.2 N NaOH	25	0.24	$6.9 \times 10^{-9}$
Gallium	0.2 N H <sub>2</sub> SO <sub>4</sub>	87	0.5	$1.6 \times 10^{-7}$
Wood's metal	"	87	0.4	$1 \times 10^{-8}$
Polished silver	"	25	0.5	$3.2 \times 10^{-8}$
Etched silver	"	..	0.5	$6 \times 10^{-7}$
Nickel *	"	25	0.52	$6 \times 10^{-7}$
Bright platinum †	"	..	0.75 to 0.3	$1.4 \text{ to } 6 \times 10^{-6}$
Lead	"	..	0.3	.....
Tantalum	"	..	0.28	.....
Copper	"	..	0.8 to 0.5	$10^{-6} \text{ to } 10^{-6}$
Bismuth ‡	"	..	0.5 to 0.4	$5 \times 10^{-12} \text{ to } 8 \times 10^{-11}$
Cobalt ‡	"	..	0.5	$10^{-8}$
			(falling)	
Antimony ‡	"	..	0.2	$2 \times 10^{-6}$
			(variable)	
Carbon	"	..	0.5	$10^{-11}$

\*  $I_0$  very independent of state of surface.

†  $\alpha$  decreased with time. Values as large as 2 have been observed.

‡ Results variable; surface possibly contaminated.

From these values the hydrogen overvoltage of a metal at any current density may be calculated. The low value of  $\alpha$  for mercury in 0.2 N sodium hydroxide suggests that the mechanism of deposition of hydrogen in alkaline solution differs from that in acid solution.

**The Influence of Other Factors on Overvoltage.** The results of Knobel and Joy's measurements<sup>2</sup> of the hydrogen overvoltage of smooth and platinized platinum, silver, copper, nickel, and lead at a number of temperatures between 0° and 75° show that with few exceptions the overvoltage decreases directly as the temperature increases. The hydrogen overvoltage of platinized platinum, however, is apparently independent of the temperature. With copper, for example, the change

<sup>1</sup> Bowden and Agar, *Ann. Repts. Chem. Soc.*, **35**, 99 (1938).

<sup>2</sup> *Trans. Am. Electrochem. Soc.*, **44**, 443 (1923).

in hydrogen overvoltage with temperature, at a current density of 0.4 ampere per square centimeter, is as follows:

Temperature:	0.4°	20.0°	47.4°	73.5°
Overvoltage:	0.572	0.508	0.456	0.395 volt

Concordant data<sup>1</sup> show that the hydrogen overvoltage of mercury decreases about 2 millivolts per degree rise in temperature. At low current densities, the influence of temperature appears to be much greater for cathodes with a low hydrogen overvoltage than for those with a high hydrogen overvoltage.<sup>2</sup> The influence of temperature at low current densities is determined mainly by the temperature coefficient of compensating processes (diffusion, chemical reaction, etc.); at high current densities, when the electrode is covered with a gas film, the predominating factor is the influence of temperature on the ease with which bubbles of gas are liberated. Accordingly, at high current densities hydrogen overvoltages and their temperature coefficients tend to become independent of the nature of the cathode material.<sup>3</sup> Fink<sup>4</sup> suggested that the slope of the overvoltage-temperature curves might have a direct bearing on whether we are dealing with a hydride or merely with occluded hydrogen. The higher the temperature, the more hydrogen evolved.

Measurements<sup>5</sup> of the hydrogen overvoltage of copper, nickel, and mercury, at pressures ranging from one atmosphere to a few centimeters of mercury, indicate that overvoltage decreases rapidly at low pressures with increase in pressure. The general form of the overvoltage-pressure curve is an hyperbola, as shown in Fig. 74.

The hydrogen overvoltage of metals is lowered by superimposing an alternating current on a direct current.<sup>6</sup> This effect is probably due to depolarization of the cathode by the oxygen set free at this electrode. The extent of this depolarization is determined primarily by the ratio of the alternating current to the direct current, and it appears to be independent of the electrode material and the current density.

Time is also a factor in overvoltage. The overvoltage of an electrode frequently increases with time, and often does not attain its maximum value until a long time after the electrode has been immersed in the electrolyte. There are some exceptions to this rule. Thus, lead and

<sup>1</sup> Glasstone, *J. Chem. Soc.*, **125**, 2414 (1924); Bircher and Harkins, *J. Am. Chem. Soc.*, **45**, 2897 (1923).

<sup>2</sup> Rideal, *J. Am. Chem. Soc.*, **42**, 94 (1920).

<sup>3</sup> Cf. Knobel, Caplan, and Eiseman, *Trans. Am. Electrochem. Soc.*, **43**, 51 (1923).

<sup>4</sup> *Ibid.*, **44**, 450 (1923).

<sup>5</sup> Goodwin and Wilson, *ibid.*, **40**, 173 (1921).

<sup>6</sup> Goodwin and Knobel, *ibid.*, **37**, 617 (1920).

mercury, metals with a high hydrogen overvoltage, acquire their maximum overvoltage almost immediately.

Theoretically, the minimum overvoltage, corresponding to the commencement of visible gas formation, should be independent of the nature

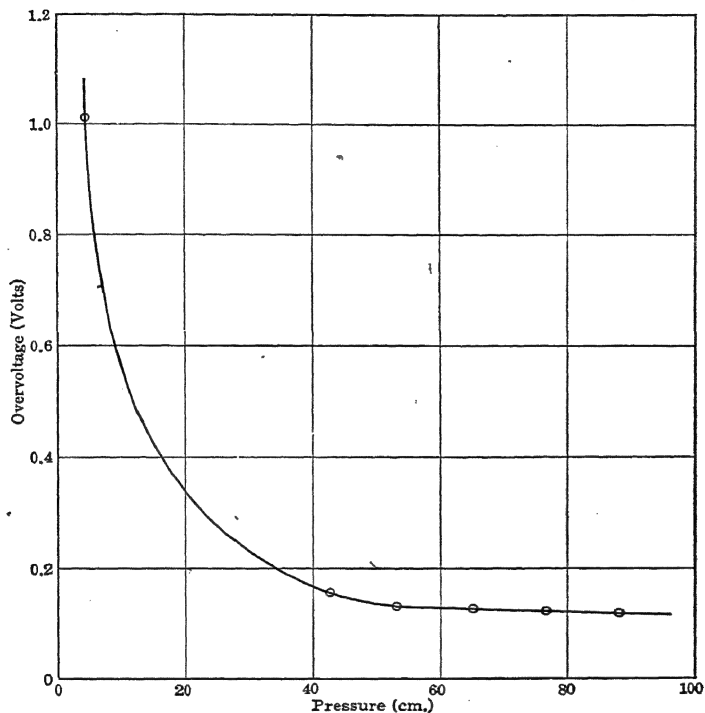


FIG. 74.

of the electrolyte. Thus, the hydrogen overvoltage of a lead cathode changes but slightly<sup>1</sup> when the hydrogen-ion concentration is varied from 1 to  $10^{-11}$ . On the other hand, the results obtained<sup>2</sup> with an antimony cathode in alkaline solutions indicate that the hydrogen overvoltage is a linear function of the difference of potential between the saturated calomel electrode and a hydrogen electrode immersed in the electrolyte. It should be pointed out that, as the hydrogen-ion concentrations of the solutions employed with the lead and antimony

<sup>1</sup> Glasstone, *J. Chem. Soc.*, **125**, 2414 (1924).

<sup>2</sup> Sand and Weeks, *ibid.*, **125**, 160 (1924).

cathodes do not overlap, the results are not necessarily contradictory. On the basis of Stern's theory of the double layer (p. 147), Frumkin has shown<sup>1</sup> that overvoltage should be independent of the hydrogen-ion concentration in pure acids, but in solutions containing an excess of foreign electrolyte it should become 0.058 volt more negative for unit increase in pH.

The influence of surface-active compounds on the hydrogen overvoltage of spongy lead in 2-8 *N* sulphuric acid has been studied.<sup>2</sup> All the compounds investigated raised the overvoltage, the increase being independent of the current density and greatest with substituted ammonium compounds. The isoamyl substituted ammonium compound gave an increase of 0.46 volt in 0.002 *M* solution; the butyl compound, 0.26 volt in 0.001 *M* solution; the propyl compound, 0.15 volt in 0.01 *M* solution.

**The Measurement of Overvoltage.** Two methods are employed for determining overvoltage. One of them consists in measuring the electrode potential while the current is flowing, by inserting the bent tube of a standard electrode in the electrolytic cell. The tip of the bent tube must be pressed against the electrode in question, so as to eliminate ohmic resistance. In the second or commutator method, the electrolyzing current is shut off momentarily (for about 0.01 second) while the potential of the electrode is determined. The potential measured by this method depends upon the concentration of the electrode products stored up during the period of electrolysis. The commutator method was employed by Newbery,<sup>3</sup> and the direct method was used by Knobel and his associates.<sup>4</sup>

Cathodic overvoltage, for example, is measured by the commutator method as follows:

A variable electromotive force is taken from the movable points  $K_3$  and  $K_4$  on the potentiometer  $P_2$  (Fig. 75), the current passing along the path  $K_3NACXMK_4$ . The current density is determined by means of the milliammeter  $M$ , and the voltage by the voltmeter  $V$ . A commutator  $X$ , rotating 2500 times a minute, makes and breaks the circuit, at the same time connecting the cathode  $C$  in a circuit containing an accurately calibrated bridge  $P_1$ , a sensitive galvanometer  $G$ , and a normal hydrogen

<sup>1</sup> *Z. physik. Chem.*, **A164**, 121 (1933).

<sup>2</sup> Vanyukova and Kabanov, *J. Phys. Chem. U.S.S.R.*, **14**, 1620 (1940).

<sup>3</sup> Cf. also Pring, *Z. Elektrochem.*, **19**, 255 (1923); Sand and Weeks, *J. Chem. Soc.*, **123**, 2896 (1923).

<sup>4</sup> Cf. also MacInnes and Adler, *J. Am. Chem. Soc.*, **41**, 194 (1919); Dunnill, *J. Chem. Soc.*, **119**, 1081 (1921); Tartar and Keyes, *J. Am. Chem. Soc.*, **44**, 557 (1922); Ferguson and Zyl, *Trans. Am. Electrochem. Soc.*, **45**, 337 (1924).

electrode *H*. A Weston cadmium cell *W* is used as a standard of electromotive force. The difference between the potential of *C* and *H*, observed and measured on the potentiometer *P*<sub>1</sub>, gives the cathodic overvoltage of the electrode *C*.

Under the same experimental conditions, the direct and commutator methods give different overvoltage values, the values determined by the

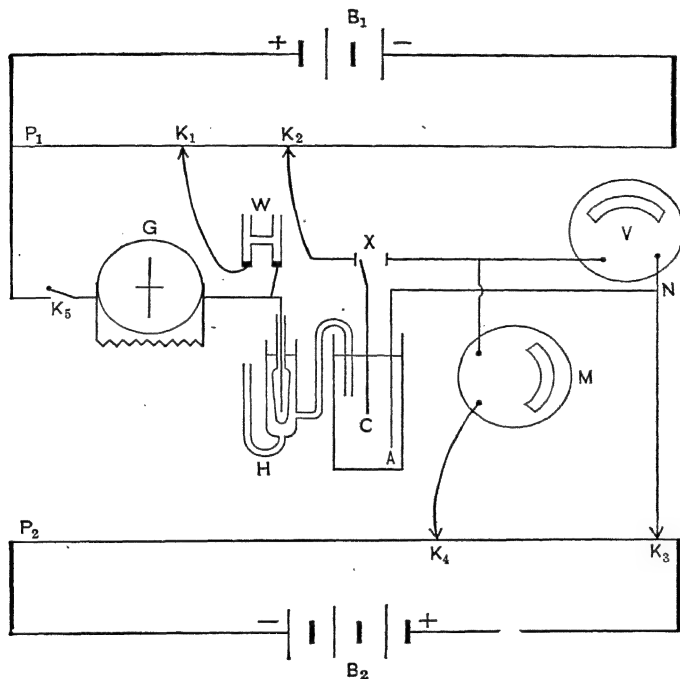


FIG. 75.

direct method invariably being the higher. There is still a considerable difference of opinion as to which method gives the true value. The objection to the direct method lies in a transfer resistance, due to a metal-gas-electrolyte system (not necessarily a gas film) at the surface of the metal, which is less than 4 ohms per square centimeter of exposed surface and which opposes the penetration of the ions into the electrode surface. The objections to the commutator method are that the fall of potential of the electrode is very rapid and that alternating induced currents lower the potential. Although the commutator method is ardently championed



by Newbery, Tartar and Keyes<sup>1</sup> conclude, from the results of a comparison of the two methods, that the commutator method gives erroneous results and that the direct method is the more accurate. The commutator method has also been criticized by other investigators.<sup>2</sup> Dunnill<sup>3</sup> found that the direct method gives the more correct results with a mercury cathode. On the other hand, Newbery<sup>4</sup> claims that no approximation to true overvoltage can be obtained without a commutator. Moreover, later experiments<sup>5</sup> show that the value of the overvoltage obtained by the direct method depends upon the size of the electrode and the concentration of the electrolyte, although the variation decreases with decrease in the current density. Although ultimately it may be found that overvoltage values obtained by neither method are correct, such values should at least be relative.

**Theories of Overvoltage.** Various theories<sup>6</sup> have been put forward from time to time to explain overvoltage. According to Newbery,<sup>7</sup> anodic overvoltage is due to the formation on the anode of higher oxides, usually stable only under the great pressures set up within the electrode during electrolysis.<sup>8</sup> The metal is assumed to absorb electrified gas, and this leaves the surface supersaturated with non-electrified gas under high pressure. Likewise, cathodic overvoltage is probably due to the high single potential of metallic hydrides formed under similar conditions. These oxides and hydrides as solid solutions would generate high back electromotive forces and would, therefore, give high oxygen and hydrogen overvoltages. The theory is supported by the following observations: (1) Frequently when the higher oxides are capable of independent existence, these oxides are actually formed at anodes of certain metals, e.g., lead dioxide at a lead anode. (2) The hydrogen liberated at an antimony cathode in acid solutions contains appreciable quantities

<sup>1</sup> *J. Am. Chem. Soc.*, **44**, 557 (1922). Cf. also Ferguson, *Trans. Electrochem. Soc.*, **76**, 113 (1939).

<sup>2</sup> Cf. MacInnes, *J. Am. Chem. Soc.*, **42**, 2223 (1920); Tainton, *Trans. Am. Electrochem. Soc.*, **41**, 389 (1922).

<sup>3</sup> *J. Chem. Soc.*, **119**, 1081 (1921).

<sup>4</sup> *J. Chem. Soc.*, **121**, 7 (1922); **125**, 511 (1924).

<sup>5</sup> Glasstone, *Trans. Faraday Soc.*, **19**, 808 (1924).

<sup>6</sup> Cf. Caspari, *Z. physik. Chem.*, **30**, 89 (1899); Bose, *ibid.*, **34**, 701 (1900); Haber, *Z. Elektrochem.*, **8**, 539 (1902); Marie, *Compt. rend.*, **147**, 1400 (1909); Möller, *Z. physik. Chem.*, **65**, 226 (1909); Reichstein, *Trans. Faraday Soc.*, **9**, 228 (1914); LeBlanc, *ibid.*, **9**, 251 (1914); Newbery, *J. Chem. Soc.*, **105**, 2419 (1914). For a review (with 75 references) see Meunier, *J. chim. phys.*, **22**, 595 (1925); also Wirtz, *Z. Elektrochem.*, **44**, 303 (1938).

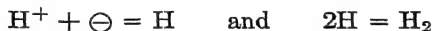
<sup>7</sup> *J. Chem. Soc.*, **109**, 1359 (1916); **125**, 511 (1924).

<sup>8</sup> The oxygen overvoltage of nickel or iron must not be confused with "passivity" of these metals (see p. 238).

of stibine; and the hydrogen set free at a carbon cathode contains hydrocarbons. (3) There are indications that copper hydride is a fairly stable compound, and that considerable quantities form on the surface of a copper cathode. When a hydride is not formed, the metal (e.g., platinized platinum) will behave merely as a reversible electrode, and the overvoltage will be zero. Foerster<sup>1</sup> also ascribes overvoltage to the formation of oxides and hydrides. Considerable experimental evidence has been obtained in support of Newbery's theory.<sup>2</sup>

Ostwald and others suggested<sup>3</sup> that the penetration of the gas into the electrode requires time, thereby causing an accumulation of gas on the surface of the electrode which generates the back electromotive force. Thus metals which do not occlude gases to an appreciable extent give high overvoltages. This view was accepted by Lewis and Jackson, who stated:<sup>4</sup>

"The theory of overvoltage, with which the authors began these experiments, was as follows: The reaction,  $2\text{H}^+ + 2\ominus = \text{H}_2$ , does not occur in a single stage, but in the two following:



The reaction whose slowness causes polarization is the second of these. In other words, the potential of a hydrogen electrode depends on the concentration of monatomic hydrogen, and this concentration increases rapidly during cathodic polarization on account of the slowness of the reaction by which it is removed. For example, at a polarization potential of 0.7 volt the concentration of this substance at the electrode would be  $10^{12}$  times as great as it would be when in equilibrium with ordinary hydrogen. Nevertheless, both of these concentrations might be absolutely very small, and probably are. The difference in polarization with different cathodes would be explained by the different catalytic action of the material at the electrode, the polarization being less the greater the catalysis. The theory, although it has been suggested by Tafel,<sup>5</sup> has had otherwise no place in the numerous discussions which the phenomenon of overvoltage has occasioned. It possesses, nevertheless, a good deal of plausibility. We may in fact cause the electrolytic reaction to proceed in the very two stages which we have written above. When

<sup>1</sup> *Z. physik. Chem.*, **69**, 236 (1909); *Z. Elektrochem.*, **16**, 353 (1910).

<sup>2</sup> Frölich and Clark, *Z. Elektrochem.*, **31**, 649 (1925); cf. also Hoar, *Proc. Roy. Soc.*, **A142**, 628 (1933).

<sup>3</sup> Ostwald, *Z. Elektrochem.*, **6**, 40 (1899); Nernst, *Theoretical Chemistry*, p. 766, 1911; Tafel, *Z. physik. Chem.*, **34**, 200 (1900); **50**, 641, 713 (1905).

<sup>4</sup> *Proc. Am. Acad. Arts Sci.*, **41**, 399 (1906); *Z. physik. Chem.*, **56**, 207 (1906).

<sup>5</sup> *Z. physik. Chem.*, **34**, 200 (1900).

hydrogen is deposited on a palladium cathode, the hydrogen, forming without marked polarization, is absorbed by the metal, where it has been shown by two independent methods<sup>1</sup> to exist in the monatomic condition. If the hydrogen is then withdrawn from the palladium, it appears in the form of ordinary hydrogen,  $H_2$ .

"But we have more striking arguments in favor of this theory. Those metals, notably platinum and palladium, in whose presence electrolytic deposition of hydrogen and the reverse reaction, the electrolytic solution of the hydrogen, progress most readily, are the very ones which we have every reason to believe catalyze the reaction  $2H \rightleftharpoons H_2$  (of course, if in one direction, in both). This reaction is doubtless a very slow one under most conditions. Hydrogen at ordinary temperatures is a pretty inert substance, but in the presence of palladium or platinum black it readily reduces a large number of substances. So, also these metals aid the union of hydrogen with other elements, such as oxygen and the halogens. Furthermore, in every known case where hydrogen is produced by a reaction, the reaction is catalyzed by these metals. We may mention the action of metals on acids, the reduction of water by chromous salts, the decomposition of a solution of sodium in liquid ammonia. It is possible that each of these reactions is catalyzed in a specific way; but it is much easier to believe that in every case the metal simply catalyzes the slow reaction,  $2H \rightleftharpoons H_2$ , and that this is also the explanation of the electrolytic reaction that we are considering. It is to be noted that metals, like mercury and lead, on which the overvoltage is highest—that is, which are the poorest catalyzers of electrolytic reaction—have little influence on any of the reactions mentioned above."

The foregoing theory was extended by Bennett and Thompson.<sup>2</sup> After showing that any chemical process cannot be strictly reversible which, in generating electricity, takes place in more than one stage, and that it is this irreversibility which gives rise to overvoltage, they proposed the following theory:

"The excess of the back electromotive force of the system during electrolysis over the reversible electromotive force of the system consisting of the final products is due to the accumulation *during such electrolysis, of unstable intermediate products above the equilibrium concentration*. These products are unquestionably active hydrogen,  $H_1$ , active oxygen,  $O_1$ , etc., in the case of gases, and  $M_1$ , atomic metal, analogous to vaporized metal, in the case of metal overvoltage. These products have been shown to be more reactive than the final product and are sufficiently active to

<sup>1</sup> Hoitsema, *Z. physik. Chem.*, **17**, 1 (1895); Winkelmann, *Drudes Ann.*, **6**, 104 (1901).

<sup>2</sup> *Trans. Am. Electrochem. Soc.*, **29**, 269 (1916); *J. Phys. Chem.*, **20**, 296 (1916).

explain overvoltages found experimentally." In accordance with this theory, the decrease of overvoltage with increase in temperature, for example, is due to an increase in the velocity of the reaction  $2\text{H}_1 \rightleftharpoons \text{H}_2$ .

By the application of quantum mechanics Gurney<sup>1</sup> has developed a mechanism of overvoltage which is regarded as a *primary* effect due to the rate of transfer of electrons between the electrode and the ions in solution, and not to secondary causes such as the accumulation of atomic hydrogen, etc., at the electrodes. According to this mechanism, oxonium ions in the vicinity of the cathode are neutralized by electrons which "leak" from the metal across the potential barrier at the cathode surface, yielding free hydrogen atoms and water molecules. Indeed, there has been considerable support for the view that the neutralization of oxonium ions by electrons, to form either free or absorbed hydrogen, may be the rate-determining process at the cathode.<sup>2</sup> The Gurney mechanism is supported by the results of kinetic studies of the establishment and decay of electrode potentials.<sup>3</sup> It has been shown<sup>4</sup> that the decay of hydrogen overvoltage at mercury electrodes is consistent with this theory when the initial potential of the electrode is not more negative than  $E_h = -1.0$  volt, and that the hydrogen formed in the electrolysis has no appreciable electromotive activity (that is, it does not yield electrons to the electrode at any appreciable rate) at potentials more negative than  $E_h = -0.33$  volt; but that the rate of decay at platinum electrodes is much more than the theoretical, indicating an accumulation at the electrode of hydrogen having electromotive activity. Hammett has found<sup>5</sup> that for large polarizations the step  $\text{H}^+ + \ominus \rightleftharpoons \text{H}$  is the dominant factor in determining the rate of hydrogen evolution, whereas for small polarizations the chief factor is the step  $2\text{H} \rightleftharpoons \text{H}_2$ . The results obtained by Cassel and Voigt<sup>6</sup> in a study of the variation of hydrogen overvoltage with pressure are in agreement with the theory that the neutralization of the ion is the chief factor which determines overvoltage.

<sup>1</sup> *Proc. Roy. Soc.*, A134, 137 (1931); A136, 378 (1932).

<sup>2</sup> Volmer and Erdey-Grúz, *Z. physik. Chem.*, A150, 203 (1930); Fowler, *Trans. Faraday Soc.*, 28, 368 (1932); Frumkin, *Z. physik. Chem.*, A160, 116 (1932); Horuti and Polanyi, *Acta Physicochim. U.R.S.S.*, 2, 505 (1935); Butler, *Proc. Roy. Soc.*, A157, 423 (1936).

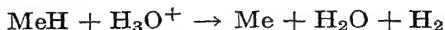
<sup>3</sup> Cf. Butler, *Trans. Faraday Soc.*, 19, 734 (1924); 28, 379 (1932); *Proc. Roy. Soc.* A137, 604 (1932); Bowden, *ibid.*, A125, 446 (1929); A126, 107 (1930).

<sup>4</sup> Butler and Armstrong, *Trans. Faraday Soc.*, 29, 1261 (1933); *J. Chem. Soc.*, 1934, 743.

<sup>5</sup> *Trans. Faraday Soc.*, 29, 770 (1933).

<sup>6</sup> *Phil. Mag.*, 16, 66 (1933).

It has been suggested <sup>1</sup> that molecular hydrogen may be formed at the cathode as the result of interaction of the hydrogen absorbed on the electrode with oxonium ions



Notwithstanding the numerous studies that have been made, no single mechanism has been proposed that explains all the features of overvoltage. Indeed, Ferguson and Bandes have presented <sup>2</sup> considerable material which supports the view that cathode overvoltage is due to more than a single factor and that the same explanation cannot apply to both the cathode and the anode.

**Electrolytic Separation of Metals.** We have seen (Table LXIV) that different electromotive forces are required to decompose aqueous solutions of different salts by electrolysis. The possibility of utilizing this behavior to separate metals quantitatively was first recognized by Freudenberg.<sup>3</sup> By employing graded electromotive forces he succeeded in effecting the separation, in acid solution, of silver from arsenic and bismuth; mercury from copper, bismuth, and arsenic; and copper and bismuth from cadmium and arsenic.

If, for example, we electrolyze a solution containing molal silver nitrate, normal cadmium nitrate, and normal lead nitrate between platinum electrodes, it is evident from the values given in Table LXIV that so long as the external electromotive force is greater than 0.70 volt and less than 1.52 volts only silver will separate at the cathode.

If, after all the silver has been separated, a new platinum cathode is placed in the electrolyte, all the lead may be separated by keeping the electromotive force between 1.52 and 1.98 volts. After all the lead has been removed from the solution, the cadmium may be separated by increasing the electromotive force to more than 1.98 volts.

The electrolytic separation of metals on this principle was described by Sand,<sup>4</sup> and much of the pioneer work was carried out by Edgar F. Smith and his students. In an analogous manner, the bromine and chlorine may be separately removed from a solution containing manganese bromide and manganese chloride.

By means of this method, known as **electroanalysis**, a large number of metals can be accurately separated and determined. The time required for analysis can be considerably shortened by employing a rotating

<sup>1</sup> Horiuti and Okamoto, *Sci. Papers Inst. Phys. Chem. Research Tokyo*, **28**, 231 (1936); Okamoto, Horiuti, and Hirota, *ibid.*, **29**, 223 (1936).

<sup>2</sup> *Trans. Electrochem. Soc.*, **81**, 289 (1942).

<sup>3</sup> *Z. physik. Chem.*, **12**, 97 (1893).

<sup>4</sup> *J. Chem. Soc.*, **91**, 373 (1907); **93**, 1572 (1908).

cathode and a high temperature, both of which help to prevent current polarization.<sup>1</sup>

For molal ionic concentrations, the separation potentials of ions are equal and opposite in sign to the values given in Table LIV, *provided that polarization does not occur*. The decomposition voltage of an electrolyte is equal to the difference of the separation potentials of its ions.

Under certain conditions the metal deposited on the cathode is non-adherent and pulverulent; under others it is adherent, smooth, and fine-grained. A knowledge of the conditions which determine the physical characteristics of the deposit is obviously of great importance in electroplating and in the electrolytic refining of metals, two very important electrochemical industries.<sup>2</sup> Among the factors which influence the characteristics of the deposit are the following:<sup>3</sup> the temperature, the current density, the concentration and circulation of the electrolyte, the chemical composition of the electrolyte, and the nature of the metal receiving the deposit. It has been found that an adherent, smooth, fine-grained deposit is more readily obtained from concentrated solutions. Consequently, the current density should be kept low, in general about 0.02 ampere per square centimeter, because otherwise the concentration of the electrolyte is too rapidly decreased in the neighborhood of the cathode. A high temperature and stirring also help to prevent a decrease in concentration near the cathode. Concentration, current density, circulation, and temperature are interdependent factors. If possible the electrolyte should be kept slightly acid, so as to prevent precipitation of basic salts or hydroxides at the cathode. Very often the characteristics of the deposit are improved by the addition of a small quantity of an organic substance, an addition agent, to the electrolyte. The presence of gas in the electrolyte is likely to cause pits in the deposited metal and sometimes renders it hard and brittle.

Hydrogen overvoltage is an important factor in the electrolytic deposition of metals. Although the separation potentials of zinc and cadmium are higher than that of hydrogen, these metals can be deposited electrolytically from a solution containing hydrogen ions whereas iron, which has a lower separation potential than either metal, cannot. This is because the liberation of hydrogen is prevented by the high hydrogen overvoltage of zinc and cadmium. On the other hand, iron has a very low hydrogen overvoltage.

When two metals are deposited electrolytically in the form of an

<sup>1</sup> E. F. Smith, *Electro-Analysis*, 1918.

<sup>2</sup> These industries are discussed by Koehler in Vol. II, Chapters V, VI, and VII.

<sup>3</sup> Cf. Watts, *Metal Ind.*, 11, 32, 83 (1913); see also Vagranian, *J. Phys. Chem. U.S.S.R.*, 10, 443 (1937).

alloy, or when a single metal forms an alloy with the cathode (e.g., with mercury), the separation potentials of the metals are decreased. This decrease, due to a decrease in the electrolytic solution pressure of the metal, often makes possible the cathodic deposition of metals having high separation potentials. Thus sodium can be deposited from an aqueous solution of sodium chloride, if a mercury cathode, which lowers the separation potential of sodium, and a high current density, which increases the hydrogen overvoltage of mercury, are employed (e.g., in the Castner-Kellner cell). Under these conditions only small quantities of hydrogen are evolved at the cathode. This behavior is of great technical importance.<sup>1</sup>

The principle of graded potentials applies to the separation of metals from fused salts as well as from aqueous solutions, there being no fundamental difference between the two cases.<sup>2</sup>

**Polarographic Analysis.** In the course of their studies of polarization phenomena, Heyrovsky and his co-workers developed a method of analysis which is based on the interpretation of current-voltage curves obtained during electrolysis.<sup>3</sup> By means of this new electroanalytical technique, known as **polarographic analysis**, ions and certain other substances can be determined both qualitatively and quantitatively at low concentrations (0.01 to 0.0001 *M*) with a sensitivity and reproducibility comparable to the optical spectrographic method. Since 1936, polarographic methods of analysis have been extensively employed in research and applied to routine analysis.

The apparatus used in polarographic analysis is represented schematically in Fig. 76.<sup>4</sup> The anode at the bottom of the electrolysis cell *D* is a pool of mercury having a large surface so as to eliminate anodic polarization; the dropping mercury electrode *K* provides a fresh cathode surface continuously. By means of the revolving potentiometer bridge *B*, actuated by the motor *A*, and supplied with current by the storage battery *H*, the voltage applied to the cell can be adjusted to any desired value. Attached to the potentiometer is a drum *C*, which carries a roll of photographic paper enclosed in a light-proof housing. The current passing through the electrolysis cell is measured by the galvanometer *G*. The movement of the galvanometer mirror reflects from a powerful source *L* a beam of light which traces a thin line on the photographic

<sup>1</sup> See Koehler, Vol. II, Chapter X.

<sup>2</sup> Drossbach, *Z. Elektrochem.*, **45**, 435 (1939).

<sup>3</sup> *Phil. Mag.*, **45**, 303 (1923). For an extensive bibliography of the work of Heyrovský and co-workers, see *Collection Czechoslov. Chem. Commun.*, **10**, 153 (1938). An excellent review of the method is given by Kolthoff and Lingane, *Chem. Revs.*, **24**, 1 (1939).

<sup>4</sup> Kolthoff and Lingane, *loc. cit.*

paper parallel to the axis of *C*. Instead of this method of recording the galvanometer movement, an arrangement of galvanometer, photoelectric relay combined with a direct-current amplifier, and recording pen, having a sensitivity of  $10^{-9}$  ampere per millimeter, has been used<sup>1</sup> to obtain the current-voltage curve directly in ink. By imposing a small alternating-current voltage on the ordinary direct-current voltage applied to the cell, the current-voltage curve can be viewed continuously on a cathode-ray oscillograph.<sup>2</sup>

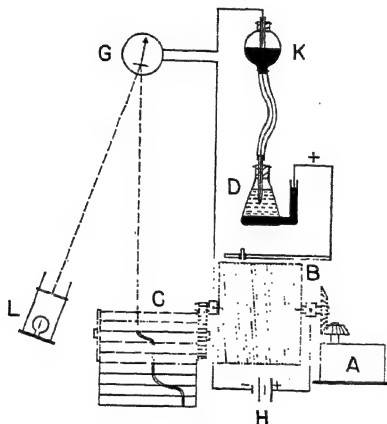


FIG. 76.

Before the solution that is to be analyzed is placed in the electrolysis cell, its resistance is made negligible by the addition of tetramethylammonium chloride, calcium chloride, potassium chloride, or other chloride having a high decomposition voltage. In consequence of this and the absence of anodic polarization, the resistance of the cell is determined almost solely by the processes which take place at the interface of the dropping mercury cathode and the solution. Accordingly, the cathode potential may be identified with the voltage of the cell, or it may be obtained more accurately by deducting from the voltage the sum of the anode potential and the potential drop through the solution.

In order to prevent its reduction at the cathode, any oxygen present in the cell is removed by a current of hydrogen bubbled through the solution prior to electrolysis.

On the application of a small voltage to the cell, a very feeble "residual

<sup>1</sup> Gull, *J. Soc. Chem. Ind.*, **56**, 177T (1937).

<sup>2</sup> Müller, Garman, Droz, and Petras, *Ind. Eng. Chem., Anal. Ed.*, **10**, 339 (1938).



current" is produced, which remains unchanged with increasing voltage until the deposition potential of some ion is reached. At this point there is a sudden, though limited, surge in the current, due to the discharge of ions at the cathode and the dissolution of mercury at the anode. Owing to the rapid depletion in the vicinity of the cathode of ions having this deposition potential, concentration polarization sets in and a "limiting current," controlled by the rate of diffusion of the depleted ion from the bulk of the solution, then passes through the cell. As the voltage is

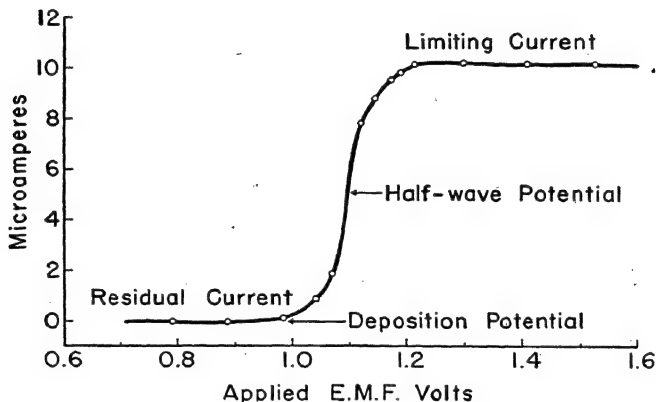


FIG. 77.

further increased, there is no change in the value of the limiting current until the deposition potential of another ion is attained. Then the behavior just described is repeated.

• The current-voltage curve, or **polarogram**, for an air-free solution of 0.0013 *M* zinc sulphate in 0.1 *N*. potassium chloride is shown in Fig. 77.<sup>1</sup> The voltage at the onset of the current surge represents a deposition potential characteristic of the zinc ion. Since the deposition potential depends to some extent on the concentration of the ion, the so-called **half-wave potential**<sup>2</sup> is found to be even more characteristic than the deposition potential. This half-wave potential is the voltage corresponding to the point on the curve (Fig. 77) where the current has one-half its limiting value. Values of half-wave potentials for a number of ions are given in Table LXXIV.<sup>3</sup> When several reducible constituents are present

<sup>1</sup> Lingane, *thesis*, 1938.

<sup>2</sup> Heyrovský and Ilkovič, *Collection Czechoslov. Chem. Commun.*, **7**, 198 (1935).

<sup>3</sup> Lingane, *loc. cit.*; Heyrovský, section on polarography in Böttger's *Die physikalischen Methoden der chemischen Analyse*, Vol. 2, pp. 260-322, 1936.

in the solution, the current-voltage curve exhibits a number of steps, each corresponding to a specific substance. This is illustrated by the polarogram (Fig. 78) obtained by electrolyzing an air-free 0.1 *M* solution of potassium chloride which contained lead nitrate, cadmium sulphate,

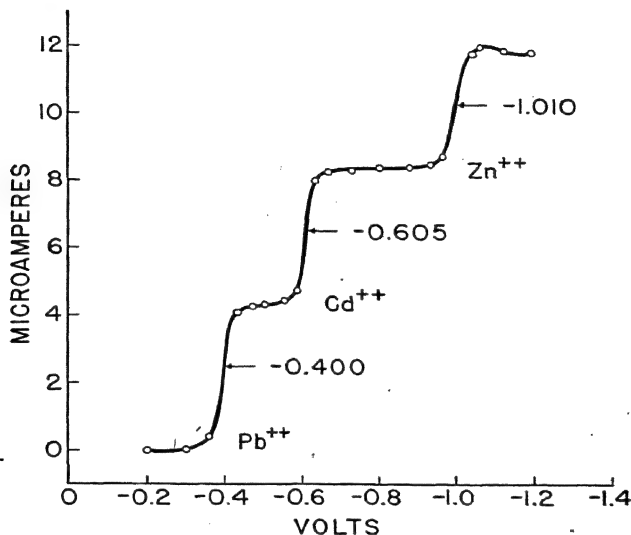


FIG. 78.

and zinc sulphate each at a concentration of 0.0005 *M*.<sup>1</sup> Owing to the high hydrogen overvoltage of mercury, the alkaline earth and the alkali metals can be deposited at the dropping mercury cathode.

TABLE LXXIV

HALF-WAVE POTENTIALS

Ion	Cu <sup>++</sup>	Pb <sup>++</sup>	Tl <sup>+</sup>	Cd <sup>++</sup>	Zn <sup>++</sup>	Na <sup>+</sup>	K <sup>+</sup>
Half-wave potential	+0.12	-0.396	-0.459	-0.599	-0.995	-2.12	-2.14

Quantitative polarographic analysis is based upon the proportionality that exists between the concentration of the depositing ion and the value of the limiting current, and it involves calibration against known standards.

**Accumulators.**<sup>2</sup> We have seen that, when an electric current from an external source is passed through certain cells, the electrodes become

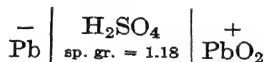
<sup>1</sup> Kolthoff and Lingane, *loc. cit.*

<sup>2</sup> For a detailed account of this subject, see Koehler, Vol. II, Chapter IV.

polarized, and that when the electrodes are connected by a wire the products of electrolysis enter the solution producing an electric current, the cell slowly returning to its original condition. Cells of this sort which can be used for the storage of electrical energy are known as **accumulators, secondary elements, or storage batteries**. Thus, the hydrogen-chlorine gas cell is a typical accumulator. Although any reversible cell could be used as an accumulator, only such combinations as retain their stored electrical energy for a long period of time when their poles are not connected, and those which are readily transported, are satisfactory from a technical standpoint. A gas accumulator would obviously not be suitable for commercial purposes. Theoretically, the Daniell cell could be used as an accumulator; actually, it is unsuited for this purpose, on account of the fact that when an electric current is sent through it the zinc is deposited in a spongy mass. Another objection to the use of this cell as an accumulator is the diffusion of the two liquids, or, if they are separated by a porous diaphragm, the high internal resistance which results.

Since accumulators are used on a large scale for the storage and transport of electrical energy, it is essential from a technical standpoint that they have a high capacity of energy per unit weight. Further, it is of the greatest importance that even slight chemical action does not occur in the accumulator when not in use, for it often has to stand idle for long periods. The conversion of electrical energy into chemical energy—called **charging**—and the subsequent transformation of chemical energy into electrical energy—called **discharging**—should be as nearly reversible as possible, so that the energy loss is a minimum. The resistance of an accumulator should be low and its construction simple.

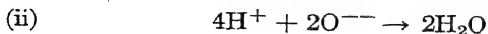
Only two accumulators have so far met with marked commercial success. These are the well-known lead accumulator or storage battery

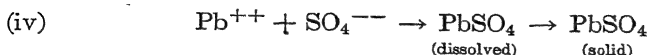
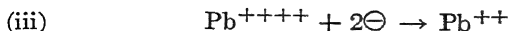


and the Edison accumulator

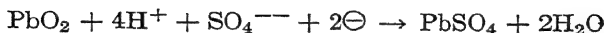


**The Lead Accumulator.** When the lead accumulator is discharged, the reactions which occur at the positive electrode may be expressed by the following equations:

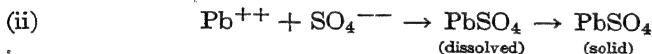




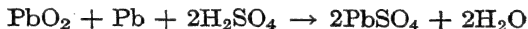
or



The reactions which occur at the negative electrode may be represented thus:

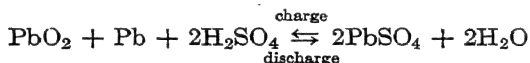


The net chemical reaction which takes place on discharging a lead accumulator may be represented thus:



When a lead accumulator is charged, the above reactions are reversed. It has been suggested<sup>1</sup> that probably some  $\text{Pb}(\text{SO}_4)_2$  is formed on the anode at the end of the charging period.

The reactions which take place when a lead accumulator is charged and discharged may be represented as follows:<sup>2</sup>



The potential of the positive electrode at room temperature is given by the expression (see equation 6, Chapter X):

$$\pi_1 = \pi^\circ_{\text{Pb}^{++++} \rightarrow \text{Pb}^{++}} + \frac{0.058}{2} \log \frac{[\text{Pb}^{++++}]}{[\text{Pb}^{++}]} \quad (3)$$

and that of the negative electrode by the expression:

$$\pi_2 = \pi^\circ_{\text{Pb}^{++} \rightarrow \text{Pb}} + \frac{0.058}{2} \log [\text{Pb}^{++}] \quad (4)$$

Accordingly, the electromotive force of a lead accumulator is

$$E = \pi_1 - \pi_2 = \pi^\circ_{\text{Pb}^{++++} \rightarrow \text{Pb}^{++}} - \pi^\circ_{\text{Pb}^{++} \rightarrow \text{Pb}} + 0.029 \log \frac{[\text{Pb}^{++++}]}{[\text{Pb}^{++}]^2} \quad (5)$$

<sup>1</sup> Kreiger, *Bull. soc. franc. élec.*, 10, 68 (1940).

<sup>2</sup> Cf. MacInnes, Adler, and Joubert, *Trans. Am. Electrochem. Soc.*, 37, 641 (1920); Knobel, *ibid.*, 43, 99 (1923).

The normal initial electromotive force of the lead accumulator is 2.05 volts. The effect of temperature on the electromotive force of lead accumulators was determined by Vinal and Altrup.<sup>1</sup> Lead accumulators run down at the rate of 1 or 2 per cent per day. When they are allowed to stand discharged, hard crystals of lead sulphate are formed

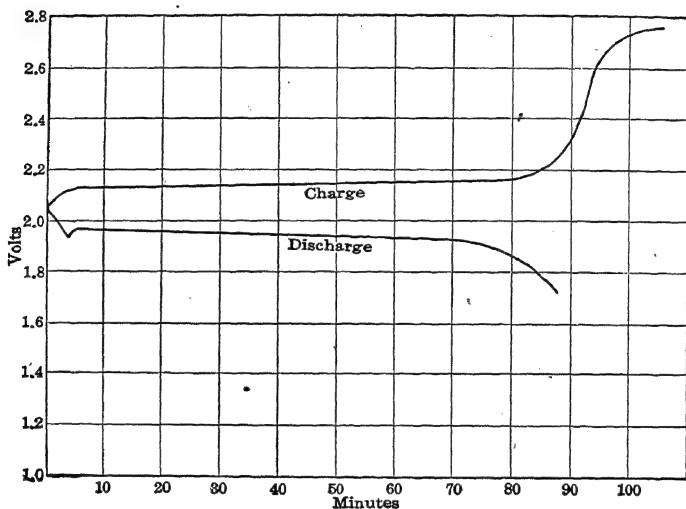


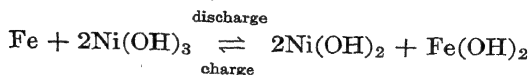
FIG. 79.

which make them very difficult to recharge. In Fig. 79 are shown the charging and discharging curves for a lead accumulator working under normal current densities.

**The Edison Accumulator.** This accumulator when charged consists of one electrode of nickelic oxide and another of iron immersed in a solution of potassium hydroxide



The reactions which take place when the accumulator is charged and discharged may be represented as follows:



<sup>1</sup> *J. Wash. Acad. Sci.*, **12**, 64 (1922).

The electrolyte undergoes no change during charging and discharging. The normal electromotive force of the Edison accumulator is 1.35 volts. The electromotive force is but slightly dependent upon the concentration of the electrolyte, as is shown by Foerster's data <sup>1</sup> in Table LXXV.

TABLE LXXV

VARIAION OF THE ELECTROMOTIVE FORCE OF THE EDISON ACCUMULATOR WITH THE CONCENTRATION OF THE ELECTROLYTE

Concentration of Electrolyte	Electromotive Force
5.3 normal	1.3349 volts
4.7 normal	1.3417 volts
2.82 normal	1.3377 volts
1.15 normal	1.3368 volts

Characteristic curves <sup>2</sup> for charging and discharging the Edison accumulator are shown in Fig. 80. These particular curves are for a 40-ampère rate. In its general form the discharge curve resembles that of

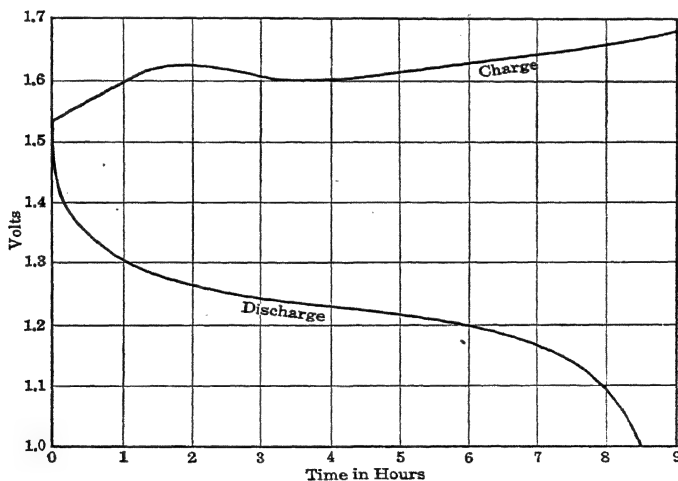


FIG. 80.

<sup>1</sup> *Z. Elektrochem.*, **14**, 285 (1908). For additional data relating to the Edison accumulator, the reader is referred to: Lyon, *J. Ind. Eng. Chem.*, **3**, 922 (1911); Bennett and Gilbert, *Trans. Am. Electrochem. Soc.*, **23**, 359 (1913; this paper gives references to the early literature); Fox, *Electrician*, **72**, 580 (1914); Turnock, *Trans. Am. Electrochem. Soc.*, **30**, 273 (1916); Thomson and Byrne, *ibid.*, **31**, 339 (1917).

<sup>2</sup> Lyon, *J. Ind. Eng. Chem.*, **3**, 927 (1911).

the lead accumulator, but the decrease in voltage is somewhat more rapid. The charge curve shows a small maximum soon after the start. There is a marked rise in temperature both on charging and discharging the Edison accumulator.

As compared with the lead accumulator, the efficiency of the Edison accumulator decreases more rapidly with decrease in the temperature of the electrolyte. Under normal conditions the ampere-hour efficiency of the Edison accumulator is about 82 per cent, and that of the lead accumulator 95 per cent. The energy, or watt-hour, efficiency of the Edison is 55 to 60 per cent; that of the lead accumulator averages about 75 per cent.

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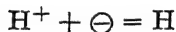
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## CHAPTER XII

### DEPOLARIZATION AND ELECTROLYSIS

**Depolarizers.** Many organic compounds act as depolarizers, when they are capable of reacting with the products formed by the discharge of the ions. **Cathodic depolarizers** are those substances which either take up hydrogen or yield oxygen, or do both simultaneously. A cathodic depolarizer is therefore reduced at the cathode during electrolysis. Thus, *o*-nitrophenol, when present in an aqueous solution of sodium hydroxide, is reduced to *o*-amidophenol at a platinum cathode.<sup>1</sup> Hydrogen peroxide is a valuable cathodic depolarizer in the electrodeposition of nickel.<sup>2</sup> **Anodic depolarizers** are oxidizable substances. Reactions which take place at the anode between the depolarizer and the discharged ions are usually much more varied than those occurring at the cathode, on account of the large variety of anions. The oxidation of hydroquinone in aqueous sulphuric acid to quinhydrone,<sup>3</sup> and the conversion of acetone to iodoform in alkaline solutions of potassium iodide, may be cited as examples of anodic depolarization.

**Electrolytic Reduction.** The electrolytic reduction of a depolarizer consists of two parts: (a) the primary process involving the discharge of hydrogen ions:



and (b) the interaction of the depolarizer and the nascent hydrogen formed in (a). Since gaseous molecular hydrogen has but little reducing power, the conditions under which the process is carried out should be such that the reaction



does not take place. Any liberation of gaseous hydrogen at the cathode during electrolysis lowers the current efficiency of the reduction of the depolarizer.

Electrochemical methods of reduction possess several advantages over purely chemical methods. For example, by varying the conditions of

<sup>1</sup> Löb, *Z. Elektrochem.*, **2**, 529 (1896).

<sup>2</sup> Madsen, *Trans. Am. Electrochem. Soc.*, **45** (1924).

<sup>3</sup> Liebmann, *Z. Elektrochem.*, **2**, 497 (1896).



electrolysis, a whole series of reduction compounds may be formed from the same depolarizer. In order to produce the same changes by chemical means, a different reducing agent would be required for each reduction product. Another advantage of the electrochemical method is that the reduction product is uncontaminated by the reducing agent (in oxidized form).

(a) *The Influence of the Cathode Potential.* The nature of the reduction which takes place with one and the same depolarizer depends very largely upon the magnitude of the cathode potential, as was shown by the classical investigation of Haber.<sup>1</sup> Indeed the effects of all other influences are contained in the cathode potential.<sup>2</sup>

The cathode potential ( $\pi$ ) is given by a modification of equation 13, Chapter VIII:

$$\pi = -RT \ln \frac{C_H \cdot k}{C_H^+} \quad (1)$$

where  $C_H^+$  is the concentration of the hydrogen ions in solution,  $C_H$  is the concentration of the active hydrogen in the electrode (proportional to the electrolytic solution pressure of hydrogen), and  $k$  is a constant. (Let the student derive equation 1.) Since  $C_H^+$  may be taken as constant, the cathode potential is proportional to the concentration of the active hydrogen. Therefore, in accordance with the law of mass action, the magnitude of the cathode potential is a measure of its reducing power; and this is greater the higher the cathode potential. Large variations in the value of the cathode potential may be obtained by regulating the current density, the temperature, the electrode material, and other conditions under which electrolysis is carried out.

Haber showed that the potential of a platinum cathode in an alkaline aqueous-alcohol solution of nitrobenzene is 0.72 volt. With cathodic polarization this rises to 1.29 volt, at which potential gaseous hydrogen is liberated. By regulating the potential between these two values, various "grades of reducing energy" are available. Thus, with a cathode potential below 0.93 volt the chief reduction product obtained in the electrolysis of the above solution is azoxybenzene, accompanied by but small quantities of azobenzene, hydrazobenzene, and aniline. With higher cathode potentials hydrazobenzene is the principal reduction compound. Hydrazobenzene is reduced further only with the greatest difficulty. These relations are comparable with those involved in the separation of metals by means of graded electromotive forces.

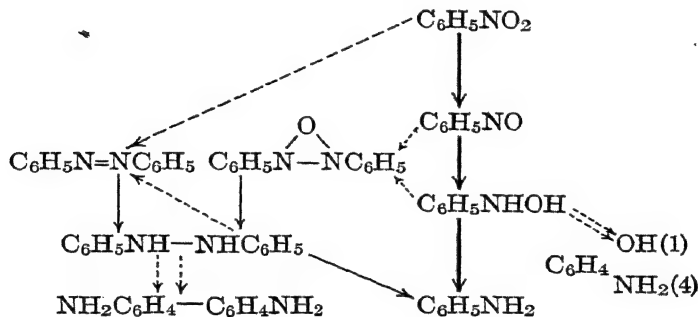
It may be inferred, from what has been said, that a substance reduced

<sup>1</sup> Z. *Elektrochem.*, **4**, 506 (1898).

<sup>2</sup> Z. *physik. Chem.*, **34**, 187 (1900); L6b and Moore, *ibid.*, **47**, 418 (1904).

at a potential only above that required for the liberation of hydrogen is of little use as a cathodic depolarizer.

From the results of his own investigations and those of earlier workers, Haber <sup>1</sup> developed the following scheme to represent the various stages of reduction of nitrobenzene, in both acid and alkaline solution under different experimental conditions. In this scheme the arrows with solid lines denote the electrochemical reductions, and those with dotted lines the purely chemical changes; the single arrows represent changes which occur in both acid and alkaline solution, and the double dotted arrows those which take place only in acid solution. Starting with nitrobenzene, the primary reduction products are denoted by the heavier vertical arrows immediately below this compound.



It will be observed that in acid solution molecular rearrangements take place, both *p*-amidophenol and benzidine being formed in this way, from phenylhydroxylamine and from hydrazobenzene, respectively. In both acid and alkaline solution azoxybenzene is formed by the pure chemical interaction of nitrosobenzene and phenylhydroxylamine, and azobenzene from nitrobenzene and hydrazobenzene in the same manner. Although the actual presence of nitrosobenzene has been confirmed by Haber, it cannot be isolated in quantity, owing to the fact that the potential of a platinum cathode in an alkaline alcoholic solution of this compound is only 0.48 volt. Hydrazobenzene is formed by the electrochemical reduction of the secondarily formed azoxybenzene.

The correctness of Haber's scheme has been demonstrated by subsequent investigators, and similar schemes have been found to hold for the electrochemical reduction of other aromatic nitro compounds.

The nature of the cathode material is an important factor in electrolytic reduction. By using a material with a high hydrogen overvoltage,

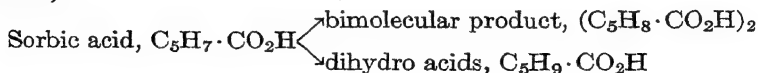
<sup>1</sup> Cf. also Nover, *Ber.*, 40, 288 (1907).

a higher cathode potential and, therefore, greater reducing energy may be obtained, without the liberation of gaseous hydrogen.<sup>1</sup> Tafel<sup>2</sup> showed that the reduction of substances like pyridine and compounds containing the keto group, reducible only with great difficulty, can be accomplished readily at cathodes of lead and mercury—metals with high hydrogen overvoltages—whereas little or no reduction takes place at a platinum cathode. Frequently, reduction proceeds further and with a higher current efficiency at a mercury than at a lead cathode. From the results of his experiments, Tafel concluded that “substances which are difficult to reduce can only be reduced in sulphuric acid solution, when such cathodes are employed as give a particularly high overvoltage.” In order to secure this high hydrogen overvoltage, it is essential that the metal of the cathode be free from impurities, as often even traces of foreign metals lower the overvoltage considerably. When lead cathodes are used in these reductions, they first must be treated electrolytically.<sup>3</sup>

It has been suggested that the cathode potential in electrochemical reduction processes can be controlled by means of a specially designed circuit.<sup>4</sup>

(b) *Physical Condition of the Cathode.* The physical condition of the cathode may exert an influence on electrochemical reduction.<sup>5</sup> In the electrochemical reduction of benzoic acid at cathodes of 99.99+ per cent lead, Swann and Lucher obtained better yields of benzyl alcohol when the metal was extruded than when it was cast; and they found that after prolonged use the activity of the cathode decreased, owing to a diminution in the crystal size of the lead surface as well as to the formation of lead sulphate. These same investigators found the yield of benzyl alcohol at a cadmium cathode to be associated with the ability of the metal to undergo a macro etch of its surface, the yield being approximately proportional to the extent of etching which the surface underwent.

The electrochemical reduction of sorbic acid may yield both dihydro acids and a bimolecular product (probably formed by the dimerization of radicals):



<sup>1</sup> Cf. Rutter, *Z. Elektrochem.*, **12**, 230 (1906); Deithelm and Foerster, *Z. physik. Chem.*, **62**, 135 (1908); Ott, *Z. Elektrochem.*, **18**, 349 (1912).

<sup>2</sup> *Z. physik. Chem.*, **34**, 187 (1900); *Ber.*, **33**, 2209 (1900).

<sup>3</sup> Cf. Tafel, *Z. physik. Chem.*, **34**, 187 (1900); *Ber.*, **33**, 2209 (1900).

<sup>4</sup> Hickling, *Trans. Faraday Soc.*, **38**, 27 (1942).

<sup>5</sup> Cf. Swann and Lucher, *Trans. Electrochem. Soc.*, **75**, 411 (1939); Wilson and Wilson, *J. Chem. Soc.*, **1941**, 874.

In a study of this reduction in alkaline solution appreciable amounts of bimolecular product were obtained only with mercury.<sup>1</sup> That this unique behavior of mercury is in some manner associated with its liquid state is supported by the fact that, while bimolecular product is formed at a solid gallium cathode, a very marked increase in its yield takes place as the temperature of this cathode passes through its melting point (29°).<sup>2</sup>

(c) *The Velocity of Depolarization.* This is another important factor in electrolytic reduction. In fact, the process of reduction depends not

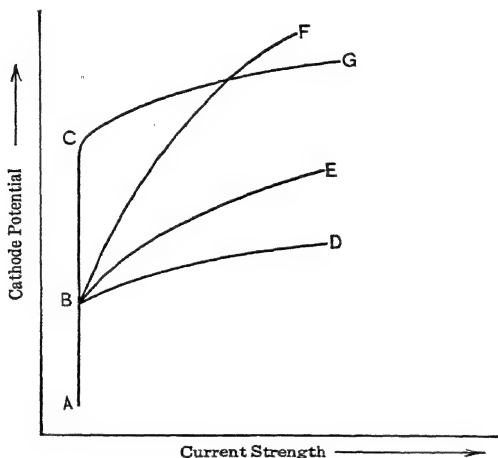
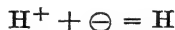


FIG. 81.

only upon the energy of reduction as measured by the cathode potential; but also upon the velocity of the secondary process. It is evident that if the reaction



is faster than the reaction between the active hydrogen and the depolarizer, the concentration of the active hydrogen will gradually increase and with it the cathode potential (see equation 1). When the

<sup>1</sup> Isaacs and Wilson, *J. Chem. Soc.*, **1936**, 202.

<sup>2</sup> Wilson, *Trans. Electrochem. Soc.*, **75**, 353 (1939). Wilson associates the increase in the yield of bimolecular product with the increase in the hydrogen overvoltage of gallium which has been found to occur during the passage from the solid to the liquid state (cf. Stelling, *Z. Elektrochem.*, **41**, 787 [1935]). It should be pointed out that Butts and Johnson (*Trans. Electrochem. Soc.*, **70**, 259 [1936]) failed to find any difference in the hydrogen overvoltage of gallium on either side of its melting point.

cathode potential becomes sufficiently high, gaseous hydrogen will be liberated at the electrode. This behavior is illustrated in Fig. 81, in which the cathode potential-current curve for hydrogen evolution is represented by *ACG*. If the solution contains a depolarizer which reacts rapidly with the active hydrogen, then the cathode potential-current curve will be represented by *ABD*. With depolarizers which react more slowly, the curve is *ABE*. Since the cathode potential rises with current density, it may happen that these curves (*ABF*) intersect the curve for hydrogen evolution when high current densities are employed. As the point of intersection of the curves corresponds to the cathode potential required for hydrogen evolution, part of the current will be consumed in producing gaseous hydrogen and the current efficiency of the reduction of the depolarizer will be diminished. *The higher the velocity of depolarization, the more efficient is the reduction of the depolarizer.*

Since a high current density not only raises the cathode potential but also decreases the concentration of the depolarizer in the vicinity of the cathode, electrolytic reduction is, in general, more rapid and complete the lower the current density. That is, a large cathode surface should be employed. Obviously, an increase in the concentration of the depolarizer will also contribute to more efficient reduction. Effective stirring is likewise advantageous.

(d) *The Influence of Catalysts.* It is sometimes possible to accelerate a slow reaction between the depolarizer and the active hydrogen by the addition of a small quantity of a substance which acts as a catalyst, and thereby to increase the efficiency of reduction. Thus, in the presence of a small quantity of titanium chloride, quinone in acid solution may be reduced to hydroquinone with a good yield at a platinum cathode.<sup>1</sup> The titanium chloride, which acts as a hydrogen carrier, is rapidly reduced at the cathode to the titano compound. This then quickly reduces the quinone to hydroquinone, titanium chloride being reformed by the reaction, and the cycle continues. The catalytic action of vanadium and iron salts is analogous to that of titanium chloride. In the presence of a catalyst the cathode potential need not be higher than that required for the reduction of the catalyst.

In addition to its hydrogen overvoltage, the catalytic action of the cathode material plays a decisive role in electrolytic reduction.<sup>2</sup> In fact, the end result of the process depends largely upon this factor. In the electrolysis of nitrobenzene in alkaline alcoholic solution, azoxybenzene, together with azobenzene, is formed at room temperature at cathodes

<sup>1</sup> Meister, Lucius, and Brüning, Ger. patent 168,273 (1903).

<sup>2</sup> Cf. Müller, *Z. anorg. Chem.*, **26**, 1 (1901); Müller and Weber, *Z. Elektrochem.*, **9**, 955 (1903).

of platinum, nickel, or mercury; under the same conditions hydrazobenzene is formed with zinc, tin, or lead; with a copper cathode the principal reduction product is aniline.<sup>1</sup> The condition of the surface of the cathode also plays a part in the reduction process. As a rule, reduction proceeds more readily and with a higher velocity when the surface of the cathode is rough or spongy than when it is smooth.

(e) *Surface-Active Agents.* Although it has been claimed that the current efficiency of depolarization can be increased by the addition of surface-active agents to the electrolyte,<sup>2</sup> there has been no general agreement whether materials of this nature have any effect, either beneficial or detrimental.<sup>3</sup> In view of this lack of agreement, a thorough study has been made<sup>4</sup> of the effect of a number of surface-active agents on the electrochemical reduction of *o*-nitrotoluene, chloropicrin, benzaldehyde, anisole, *m*- and *p*-tolualdehydes, acetophenone, and pyrrole. The effect of every one of these substances was to bring about a decrease in the current efficiency of reduction. The surface-active agents which produced the greatest decrease in the efficiency were those which were most active in producing foaming in the electrolyte. With agents of the anion type, the detrimental effect increased with increase in the concentration of the agent; with agents of the cation type, a large inhibiting effect occurred at low concentrations of the agent, but subsequent additions were without further influence. The decrease in the current efficiency is attributed to either (1) the stabilization of emulsions of organic liquids in aqueous solution by the surface-active agent of the anion type or (2) the exclusion of the depolarizer from the reducing zone of the cathode, due to the saturation of the electrode surface by an agent of the cation type.

(f) *Applications of Electrochemical Reduction.* In the practical application of electrochemical reduction, it must be remembered that the products formed at the cathode are likely to be oxidized at the anode. In order to prevent this from happening, the anode is frequently separated from the cathode by a diaphragm.<sup>5</sup> The portions of electrolyte contained in the sections thus formed are termed the **anolyte** and **catholyte**, respectively. The same end can sometimes be attained by employing a high anodic current density (i.e., a small anode surface) or, in alkaline solutions, iron or nickel anodes—metals with the smallest oxygen over-voltages.

<sup>1</sup> Löb, *Z. Elektrochem.*, **8**, 778 (1902).

<sup>2</sup> Cf. Kyrides and Bertsch, U. S. patent 1,927,289 (1933); Fichter, *Helv. Chim. Acta*, **18**, 831 (1935).

<sup>3</sup> Cf. Mitchell, *Trans. Electrochem. Soc.*, **56**, 495 (1929).

<sup>4</sup> Proudfit and France, *J. Phys. Chem.*, **46**, 42 (1942).

<sup>5</sup> The author has found diaphragms made of Alundum to be most satisfactory.

A large number of organic compounds have been prepared by electrochemical reduction processes.<sup>1</sup> In addition to the types of reduction already discussed, the following may be mentioned: The reduction of aromatic nitro compounds yields many and varied products.<sup>2</sup> Like nitro compounds, substances containing the carbonyl group are readily reduced in both acid and alkaline solution, and many compounds have been prepared electrochemically from aldehydes, ketones, carboxylic acids (particularly their esters), acid amides, and imides.<sup>3</sup> The addition of hydrogen to organic compounds may be effected. Thus, tetrahydrobenzoic acid has been prepared from benzoic acid in alkaline solution at a mercury cathode; piperidine from pyridine; and indigo white from indigo. Of this type of reduction, the conversion of oleic to stearic acid,<sup>4</sup> and the reduction of sugars to their corresponding alcohols,<sup>5</sup> are of technical interest.

**Electrolytic Oxidation.** The principal types of electrolytic oxidation involve the discharge of hydroxyl ions



or the discharge of halogen ions. The process is analogous to electrolytic reduction, and the same general considerations apply to both.<sup>6</sup>

In electrolytic oxidation the number of electrode materials (anode) is more limited than in reduction processes. Since, in general, it is important that the anode should be attacked as little as possible during electrolysis, we are confined to the use of platinum, iridium, palladium, carbon, iron, and nickel for processes that take place in alkaline solution, and to the platinum metals and carbon for those carried out in acid solution. Anodes of lead dioxide may be employed in sulphuric acid

<sup>1</sup> For a résumé of the applications of electrochemical reduction, see Aten, *Chem. Weekblad*, **19**, 349 (1922); Swann, *Trans. Electrochem. Soc.*, **69**, 287 (1936); **77**, 459 (1940).

<sup>2</sup> Cf. Elbs, *J. prakt. Chem.*, **43**, 39 (1891); *Z. Elektrochem.*, **7**, 133, 141 (1900); **9**, 727 (1903); **12**, 685 (1906); **13**, 639 (1907); **16**, 138 (1910); **18**, 665 (1912); Gattermann, *Ber.*, **26**, 1844 (1893); **29**, 3034, 3037, 3040 (1896); A. A. Noyes and Clement, *ibid.*, **26**, 990 (1893); Löb, *Z. Elektrochem.*, **2**, 529 (1896); **3**, 45 (1896); **4**, 428 (1898); **5**, 456 (1899); **7**, 320, 333 (1900); Haber, *ibid.*, **4**, 506 (1898); Chilesotti, *ibid.*, **7**, 768 (1901); Inoue, *J. Chem. Soc. Japan*, **24**, 464 (1921).

<sup>3</sup> Cf. Swann and co-workers, *Trans. Electrochem. Soc.*, **62**, 177 (1932); **67**, 195, 201 (1935); **72**, 327 (1937); **79**, 83 (1941); Wilson and Wilson, *ibid.*, **80**, 151 (1941).

<sup>4</sup> Petersen, *Z. Elektrochem.*, **11**, 549 (1905).

<sup>5</sup> Creighton, U. S. patents 1,612,361 (1926); 1,990,582 (1935); *Trans. Electrochem. Soc.*, **75**, 289 (1939); *Can. Chem. Process Inds.*, **26**, 690 (1942).

<sup>6</sup> For recent contributions to the theory of electrolytic oxidation, the reader is referred to Müller and Rius, *Z. Elektrochem.*, **27**, 54 (1921); Fichter, *ibid.*, **27**, 487 (1921); Müller, **28**, 101 (1922); Glasstone and Hickling, *Trans. Faraday Soc.*, **31**, 1656 (1935); Hickling, *J. Chem. Soc.*, **1936**, 1453; Gross and Hickling, *ibid.*, **1937**, 325.

solutions. Of these anodes, iron and nickel have the lowest oxygen overvoltages. For general work, the most suitable anodes are: (1) lead, for sulphate solutions; (2) Acheson graphite, for chloride solutions; and (3) pure nickel or a high-nickel steel for alkaline solutions.

The substances most used as catalysts—or oxygen carriers—in electrolytic oxidation are cerium, manganese, titanium, and vanadium salts, and ferricyanides and chromates. Of these, the cerium salts are the most active. For example, although but a very small amount of oxidation occurs when a suspension of anthracene in aqueous sulphuric acid is electrolyzed, if a very small quantity of cerium sulphate is added to the mixture, anthraquinone is formed with a current efficiency of 80 per cent.<sup>1</sup> The action of these catalysts is similar to that of titanium chloride in the reduction of quinone.

In the practical application of electrolytic oxidation, it is necessary to prevent cathodic reduction of the products of oxidation. This may be accomplished by the use of a diaphragm, a cathode material of low hydrogen overvoltage, or a high cathodic current density (i.e., a small cathode surface), or, sometimes, by the addition of a small quantity of potassium chromate to the electrolyte. The efficacy of potassium chromate in lessening cathodic reduction is attributed to the formation of a thin diaphragm of insoluble chromium chromate about the cathode, which prevents most of the solution from coming in contact with this electrode.<sup>2</sup>

**Applications of Electrolytic Oxidation.** Although aliphatic hydrocarbons are not readily oxidized by electrochemical methods, Coehn and Billitzer<sup>3</sup> succeeded in obtaining formic acid from acetylene in alkaline solution.<sup>4</sup> With an anode potential of 1.35 volts, the reaction proceeds almost quantitatively in accordance with the equation



By electrolyzing a suspension of benzene in dilute sulphuric acid, the hydrocarbon can be transformed to hydroquinone<sup>5</sup> or directly to quinone.<sup>6</sup> In the presence of an oxygen carrier naphthalene, suspended in sulphuric acid, is easily oxidized to naphthaquinone or to phthalic acid, depending upon the duration of electrolysis.<sup>7</sup>

<sup>1</sup> *Elektrochem. Ind.*, **2**, 249 (1904).

<sup>2</sup> Cf. Müller, *Z. Elektrochem.*, **5**, 469 (1899); **7**, 398 (1901); **8**, 909 (1902).

<sup>3</sup> *Z. Elektrochem.*, **7**, 681 (1901).

<sup>4</sup> At Shawinigan Falls, acetone is produced commercially from acetylene.

<sup>5</sup> Gattermann and Friedericks, *Ber.*, **27**, 1942 (1894).

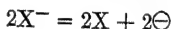
<sup>6</sup> Kempf, Ger. patent 117,251 (1899).

<sup>7</sup> Meister, Lucius, and Brünig, Ger. patent 152,063 (1902); cf. also White and Lowy, *Trans. Electrochem. Soc.*, **62**, 223 (1932).

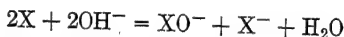


Numerous electrolytic oxidation experiments have been carried out with all classes of organic compounds. For example, aniline has been oxidized to aniline black,<sup>1</sup> hydroquinone,<sup>2</sup> quinone,<sup>3</sup> or *p*-amidophenol,<sup>4</sup> according to the conditions employed; toluene to benzaldehyde,<sup>5</sup> and *o*-toluenesulfamide to saccharine.<sup>6</sup> Although it has been claimed<sup>7</sup> that vanillin may be prepared from isoeugenol by electrochemical oxidation, Lowy and Moore<sup>8</sup> have shown that under the conditions specified an appreciable amount of vanillin cannot be obtained, on account of the ease with which it undergoes further oxidation. The electrochemical oxidation of glucose has been successfully worked out,<sup>9</sup> and this has led to the development of a process by which gluconic acid is being produced in commercial quantities.

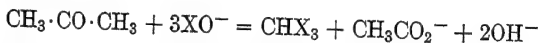
When an alkali halide is electrolyzed in the presence of organic compounds, substitution of the halogen in the organic molecule often takes place. This is an important type of electrochemical oxidation. When an aqueous alkaline solution containing alcohol or acetone is electrolyzed, chloroform, bromoform, or iodoform results, depending on the halide employed.<sup>10</sup> The first stage of this process consists in the formation of the  $\text{XO}^-$  ion (where X denotes the halogen):



and



This ion then reacts with the alcohol or acetone to form the halogen substitution product. With acetone the secondary reaction is expressed by the equation



<sup>1</sup> Coquillion, *Compt. rend.*, **81**, 408, **82**, 228 (1875).

<sup>2</sup> Ger. patent 172,654 (1903).

<sup>3</sup> Elbs, *Chem. Ztg.*, **17**, 210 (1893); Inoue and Shikata, *J. Chem. Soc. Japan*, **24**, 567 (1921).

<sup>4</sup> Vinal, Eng. patent 573 (1902).

<sup>5</sup> Law and Perkins, *Trans. Faraday Soc.*, **1**, 31 (1904).

<sup>6</sup> Ger. patent 85,491 (1895).

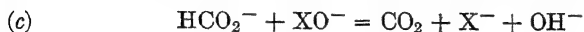
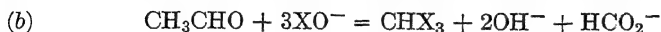
<sup>7</sup> Ger. patent 92,007 (1895).

<sup>8</sup> *Trans. Am. Electrochem. Soc.*, **42**, 273 (1922). See also *ibid.*, **45** (1924), symposium on organic electrochemistry.

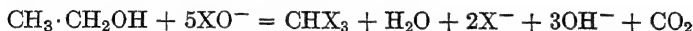
<sup>9</sup> Fink and Summers, *Trans. Electrochem. Soc.*, **74**, 625 (1938).

<sup>10</sup> Cf. Elbs and Herz, *Z. Elektrochem.*, **4**, 113 (1897); Foerster and Meves, *ibid.*, **4**, 268 (1897); Coughlin, *Am. Chem. J.*, **27**, 63 (1902); Abbot, *J. Phys. Chem.*, **7**, 84 (1904); Teeple, *J. Am. Chem. Soc.*, **26**, 170, 536 (1904); Müller and Loebe, *Z. Elektrochem.*, **10**, 409 (1904); Roush, *Trans. Am. Electrochem. Soc.*, **8**, 283 (1905); Wäser, *Chem. Z.*, **34**, 141 (1910).

According to Feyer,<sup>1</sup> with alcohol aldehyde is formed as an intermediate product in the secondary reaction



The net change is expressed by the equation



Iodoform is prepared commercially by the electrolytic method just outlined, with a 98 per cent yield, whereas by the chemical method the yield is only from 20 to 30 per cent.

Substitution also takes place when a solution containing an aromatic amine and sodium nitrite is electrolyzed with a platinum anode.<sup>2</sup> Though a diazo compound is probably formed, it has not been possible to isolate it. However, on adding a phenol to the solution, the phenol combines with the diazo compound before it can be changed in any other way, and the corresponding dye is formed.

**The Electrolysis of Ionized Substances.** Oxidations and reductions frequently take place when solutions of single electrolytes are electrolyzed, provided that the ions can undergo these changes. The simplest processes of this kind consist in: (a) a decrease or increase in the valence of the ion, and (b) the change of a cation to an anion, or *vice versa*. As examples of (a) may be mentioned the oxidation of manganates to permanganates,<sup>3</sup> of carbonates to percarbonates,<sup>4</sup> of borates to perborates,<sup>5</sup> and of chlorates to perchlorates;<sup>6</sup> and of (b), the conversion of manganese sulphate to permanganic acid in sulphuric acid solution.<sup>7</sup> The regeneration of spent chromic acid is carried out on a large scale.

<sup>1</sup> *Z. Elektrochem.*, **25**, 115 (1919).

<sup>2</sup> Löb, *ibid.*, **10**, 237 (1904). Cf. also Krauss, *J. Am. Chem. Soc.*, **39**, 1427 (1917).

<sup>3</sup> Cf. Brand and Ramsbottom, *J. prakt. Chem.*, **82**, 336 (1910).

<sup>4</sup> Cf. Constam and Hansen, *Z. Elektrochem.*, **3**, 137, 145 (1896); LeBlanc and Zellmann, *ibid.*, **29**, 179, 192 (1923).

<sup>5</sup> Cf. Tanatar, *Z. physik. Chem.*, **26**, 132 (1898); **29**, 162 (1899); Polack, *Z. Elektrochem.*, **21**, 253 (1915); Arndt, *ibid.*, **22**, 63 (1916); Arndt and Hantge, *ibid.*, **28**, 263 (1922); Alsgaard, *J. Phys. Chem.*, **26**, 137 (1922); LeBlanc and Zellmann, *loc. cit.*; Culbertson and Teach, *Trans. Electrochem. Soc.*, **81**, 191 (1942).

<sup>6</sup> Cf. Winteler, *Z. Elektrochem.*, **5**, 49, 217 (1898); **7**, 635 (1901); Bennett and Mack, *Trans. Am. Electrochem. Soc.*, **29**, 323 (1916).

<sup>7</sup> Cf. Elbs, *Z. Elektrochem.*, **7**, 260 (1900); Wilson and Horsch, *Trans. Am. Electrochem. Soc.*, **35**, 371 (1919); Thompson, *Chem. Met. Eng.*, **21**, 680 (1919); Wilson, Horsch, and Youtz, *J. Ind. Eng. Chem.*, **13**, 763 (1921).

Anions containing oxygen, especially the nitrate ion, are readily reduced at the cathode. Nitric acid is probably reduced through the stages  $\text{HNO}_3 \rightarrow \text{NO}_2 \rightarrow \text{HNO}_2 \rightarrow \text{NO} \rightarrow \text{H}_2\text{NOH} \rightarrow \text{NH}_3$ , the nature of the reduction product depending on the cathode potential, temperature, current density, concentration of the acid, and the material of the cathode. As early as 1839, Schönbein<sup>1</sup> observed that nitric acid was reduced at the cathode when the acid was concentrated, and that current density played a role; later Brewster<sup>2</sup> found that during the electrolysis of dilute nitric acid ammonia was produced at the cathode. Subsequently, Ihle<sup>3</sup> showed, for a definite concentration of nitric acid, that both ammonia and hydroxylamine are formed at a smooth platinum cathode when the current density is above a definite value, and that this value increases with the concentration of the acid. At different acid concentrations the minimum current density is:

Concentration of $\text{HNO}_3$	14.67	28.73	43.34	85.37 per cent
Current density	0.15	1.112	5.64	860.0 amp/dm <sup>2</sup>

Under otherwise favorable conditions, the relative amounts of hydroxylamine and ammonia that are formed depend largely on the nature of the cathode material. Tafel<sup>4</sup> found that, whereas nitric acid (in 50 per cent sulphuric acid) is reduced to only hydroxylamine at a mercury cathode, it is converted to chiefly ammonia at a copper cathode. The variation in the relative amounts of hydroxylamine and ammonia obtained with different cathode materials when the current density was 24 amperes per square decimeter is shown in Table LXXVI. At cathodes of carbon, graphite, and platinum, nitric acid is largely reduced to pure nitric oxide.

When nitric acid is electrolyzed between platinum electrodes in a cell containing a diaphragm, nitric oxide is formed at the cathode and oxygen is evolved at the anode. The net change in the anode section of the cell is an increase in the concentration of the acid, due not only to the loss of one-half mole of water, but also to a gain of about 0.18 mole ( $n_c = 0.82$ ) of nitric acid, per faraday of electricity passed through the cell. By electrolyzing nitric acid in this way, and passing the nitrous gases formed in the cathode section into the solution in the anode section, Creighton<sup>5</sup> was able to increase the concentration of the nitric acid from 71 to more than 99 per cent.

<sup>1</sup> *Pogg. Ann.*, **47**, 563 (1839).

<sup>2</sup> *Arch. de Genève*, **28**, 60 (1866).

<sup>3</sup> *Z. physik. Chem.*, **19**, 572 (1895).

<sup>4</sup> *Z. anorg. Chem.*, **31**, 289 (1902).

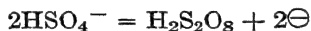
<sup>5</sup> *J. Franklin Inst.*, **193**, 89 (1922).

TABLE LXXVI

AMOUNTS OF HYDROXYLAMINE AND AMMONIA FORMED WITH DIFFERENT CATHODES

Cathode Material	Current Yield	
	Hydroxylamine	Ammonia
Copper (spongy)	1.5	95.8
Copper (polished)	11.5	76.8
Lead (rough)	26.8	57.6
Zinc (polished)	45.8	38.3
Lead (amalgamated)	69.7	19.9

Sometimes the discharged anions polymerize. Thus, when a cold solution of concentrated sulphuric acid is electrolyzed between platinum electrodes with a high current density, persulphuric acid is formed: <sup>1</sup>



Alkali persulphates can be formed in an analogous manner.<sup>2</sup>

Metallic hydroxides may be formed electrolytically, by electrolyzing an alkali chloride between a platinum cathode and an anode of the metal in question. During electrolysis the metal enters the solution at the anode in the form of ions, which react with the hydroxyl ions produced at the cathode. Similarly, metallic sulphides may be produced by electrolyzing an alkali chloride, nitrate, or sulphate between an anode of the metal and a cathode of copper sulphide. In this case, sulphur ions are formed at the cathode.

The electrolytic formation of hypochlorites, chlorates, and alkali hydroxides by the electrolysis of aqueous solutions of alkali chlorides, and of metallic sodium hydroxide by the electrolysis of fused sodium chloride, will be considered in Vol. II.

Although the potentialities of electro-organic chemistry were first recognized by Faraday,<sup>3</sup> it was Kolbe who laid the foundations of modern electro-organic synthesis and discovered the well-known synthesis of

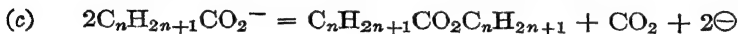
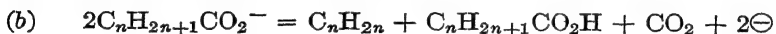
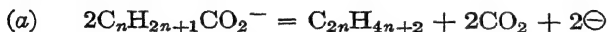
<sup>1</sup> Cf. Marshall, *J. Chem. Soc.*, **59**, 771 (1891); Elbs and Schönherr, *Z. Elektrochem.*, **1**, 417, 468 (1895); **2**, 245 (1895); Müller and Schellhaus, *ibid.*, **13**, 257 (1907); Schellhaus, *ibid.*, **14**, 121 (1908); Anders, dissertation, Dresden, 1913.

<sup>2</sup> Cf. Marshall, *loc. cit.*, and *J. Soc. Chem. Ind.*, **16**, 396 (1897).

<sup>3</sup> *Pogg. Ann.*, **33**, 450 (1834).

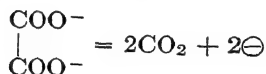
aliphatic hydrocarbons which bears his name.<sup>1</sup> Practically all the reactions which take place during the electrolysis of salts of aliphatic acids occur at the anode, for, with the exception of a relatively small number of organic bases, the cations of organic electrolytes do not usually take part in any reaction at the cathode. Many electrochemical organic reactions are possible, owing to the very large number of anions.

Although oxygen is usually produced at the anode when dilute solutions of aliphatic monobasic acids or their salts are electrolyzed, with concentrated solutions and a high current density, in general, union takes place between the discharged anions, which is followed by a splitting off of carbon dioxide from the new molecule. The different types of reactions which may occur under these conditions are represented by the following equations:



Which one of these reactions takes place depends largely upon the nature of the anion and but slightly upon the experimental conditions. With potassium acetate, ethane and carbon dioxide are formed;<sup>2</sup> with salts of propionic and butyric acids the anode reaction corresponds to (b);<sup>3</sup> with trichloroacetic acid reaction (c) predominates.<sup>4</sup> As a rule, the salts of aromatic monobasic acids yield only oxygen at the anode. Notwithstanding many attempts, it was not until 1939 that a Kolbe synthesis was successfully carried out with salts of aromatic acids.<sup>5</sup>

Electrolysis of salts of dibasic acids results merely in oxidation and not in synthesis. For example, with potassium oxalate, carbon dioxide is the sole product formed at the anode:<sup>6</sup>



<sup>1</sup> *Lieb. Ann.*, **69**, 257 (1849).

<sup>2</sup> Kolbe, *loc. cit.*; Murray, *J. Chem. Soc.*, **61**, 10 (1892); Petersen, *Z. physik. Chem.*, **33**, 90 (1900). The mechanism of the Kolbe synthesis has been discussed by Glasstone and Hickling, *Trans. Electrochem. Soc.*, **75**, 333 (1939).

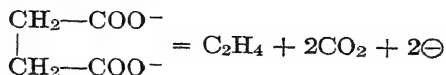
<sup>3</sup> Petersen, *loc. cit.*

<sup>4</sup> Elbs, *J. prakt. Chem.*, **55**, 502 (1897).

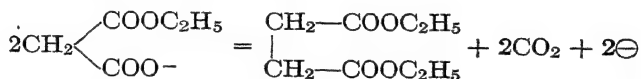
<sup>5</sup> Fichter and Stenzl, *Helv. Chim. Acta*, **22**, 970 (1939).

<sup>6</sup> Petersen, *loc. cit.*

with an alkali succinate the anode products are ethylene and carbon dioxide:<sup>1</sup>



On the other hand, by electrolyzing the acid esters of dibasic acids Crum Brown and Walker<sup>2</sup> succeeded in producing a variety of synthetic products. Thus, diethylsuccinate is formed when the potassium salt of ethyl malonic acid is electrolyzed:



The low solubility of the depolarizer in water frequently presents a difficulty in the electrolytic reduction or oxidation of organic substances. McKee and his associates have found,<sup>3</sup> however, that saturated aqueous solutions of the sodium salts of organic acids of high molecular weight may be successfully employed as solvents for many organic compounds which are rather insoluble in water.

**Deuterium and Deuterium Oxide.** In 1932 the existence of deuterium (D), an isotope of hydrogen having a mass of 2, was discovered by Urey, Brickwedde, and Murphy.<sup>4</sup> The oxide of this element, the so-called heavy water, is present in ordinary water to the extent of 1 part in 5750.<sup>5</sup>

Of the various methods of preparing deuterium oxide, the fractional electrolysis of aqueous solutions of sodium or potassium hydroxide is the only one that has been extensively employed for the systematic concentration of large quantities of heavy water.<sup>6</sup> It has been shown<sup>7</sup> that the separation of the hydrogen isotopes by fractional electrolysis cannot depend on differences of the electrode potentials of the hydrogen and deuterium ions, since these are very small, but must be due to causes such as differences in the rates of combination of the hydrogen and the deuterium atoms on the electrodes, or the greater mobility of the lighter ion. Bell and Wolfenden conclude<sup>8</sup> that the efficiency of the separation

<sup>1</sup> Petersen, *loc. cit.*

<sup>2</sup> *Lieb. Ann.*, **261**, 107 (1891); **274**, 41 (1893).

<sup>3</sup> McKee and Brockman, *Trans. Electrochem. Soc.*, **62**, 203 (1932); McKee and Heard, *ibid.*, **65**, 301, 327 (1934).

<sup>4</sup> *Phys. Rev.*, **40**, 1 (1932).

<sup>5</sup> Johnston, *J. Am. Chem. Soc.*, **57**, 484 (1935).

<sup>6</sup> Cf. Lewis and Macdonald, *J. Chem. Phys.*, **1**, 341 (1933).

<sup>7</sup> Urey and Rittenberg, *ibid.*, **1**, 137 (1933).

<sup>8</sup> *Nature*, **132**, 931 (1933); cf. Fowler, *Proc. Roy. Soc.*, **A144**, 452 (1934).

depends primarily on the greater speed with which the lighter ion picks up electrons from the cathode.

Measurements have been made at 18° of the mobility of the deuterium, potassium, and chlorine ion in deuterium oxide by Lewis and Doody,<sup>1</sup> who obtained the values 213.7, 54.5, and 55.3, respectively. The values of the mobility of the hydrogen, potassium, and chlorine ion in water at 18° are given in Table XXXVII.

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### PROBLEMS

1. Given that the current efficiency of the electrolytic reduction of nitrobenzene to azobenzene is 80 per cent, how many coulombs of electricity will be required for the transformation of 20 grams of nitrobenzene into azobenzene?
2. If, in the preceding problem, the potential difference between the electrodes were 3.7 volts, calculate the electrical energy consumed per kilogram of azobenzene produced.
3. On electrolyzing a solution of ammonium acid sulphate at a temperature of 5°, the potential difference between the electrodes is 7 volts. Given that ammonium persulphate is formed with a current efficiency of 74 per cent, calculate the electrical energy required to produce 10 liters of a solution containing 10 per cent of the salt.

<sup>1</sup> *J. Am. Chem. Soc.*, **55**, 3504 (1933).

## CHAPTER XIII

### THE APPLICATION OF THE LAW OF MASS ACTION TO ELECTROLYTIC DISSOCIATION

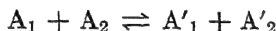
According to the law of mass action, the velocity of a chemical reaction is directly proportional to the product of the concentrations, or the active masses, of the reacting substances. Thus the velocity ( $u$ ) of the reaction



is given by the expression

$$u = k[A] \quad (1)$$

where  $k$  is a constant—the so-called **velocity constant**. In the reversible change



the velocity of the reaction from left to right is given by

$$u_1 = k_1[A_1][A_2] \quad (2)$$

and that of the reverse reaction by

$$u_2 = k_2[A'_1][A'_2] \quad (3)$$

Since at equilibrium the velocities of the opposing reactions are equal, we may write

$$K = \frac{k_1}{k_2} = \frac{[A'_1]_e[A'_2]_e}{[A_1]_e[A_2]_e} \quad (4)$$

where the subscript  $e$  denotes the equilibrium concentration of the reacting substances. The constant  $K$  is the so-called equilibrium constant (cf. equation 22, Chapter VIII). This general equation is applicable to all chemical equilibria in gaseous and liquid systems.

**Ostwald's Dilution Law.** We have seen that when a weak electrolyte is dissolved in water there exist in solution both ions and undissociated molecules, the concentration of the undissociated molecules being much the greater. If solvent is withdrawn from the solution, some of the ions combine to form undissociated molecules, as indicated by a decrease in the value of the conductance ratio,  $\Lambda_c/\Lambda_0 = \alpha$ ; if solvent is added to



the solution, the reverse process occurs. Electrolytic dissociation of these electrolytes is, therefore, a reversible process. At a definite temperature and concentration the degree of dissociation of an electrolyte is constant, and a definite equilibrium exists between the ions and the undissociated molecules. Consequently, the law of mass action, as expressed by equation 4, should be applicable to electrolytic equilibria.

Let us consider a solution of a weak binary electrolyte, MA, having a concentration of  $c$  equivalents per liter, which dissociates in accordance with the equation



If at the concentration  $c$  the degree of dissociation, or the fraction of each mole of electrolyte that is ionized, is represented by  $\alpha$ , then the equilibrium concentration of the undissociated molecules will be  $(1 - \alpha)c$  equivalents per liter, and that of each kind of ion will be  $\alpha c$  equivalents per liter. On substituting these values in equation 4, we obtain:

$$\frac{\alpha c \cdot \alpha c}{(1 - \alpha)c} = K$$

or

$$\frac{\alpha^2 c}{(1 - \alpha)} = K \quad (5)$$

where  $K$ , the equilibrium constant, or the **dissociation constant**, is characteristic of the electrolyte for a definite temperature and solvent. This equation, which expresses the relation between the degree of dissociation and the concentration of an electrolyte, was first derived by Ostwald.<sup>1</sup> It is known as Ostwald's **dilution law**. Expressed in words, the law states that the product of the concentrations of the ions divided by the concentration of the undissociated molecules is a constant quantity; i.e.,

$$\frac{(\text{Concn. of cations})(\text{Concn. of anions})}{(\text{Concn. of undissociated molecules})} = \text{Dissociation constant} \quad (6)$$

If the degree of dissociation of an electrolyte is known, or can be determined, for a particular concentration, its dissociation constant may be calculated by means of equation 5; and with the value of  $K$  thus obtained the degree of dissociation corresponding to other concentrations may be calculated. On solving equation 5 for  $\alpha$ , we obtain:

$$\alpha = \frac{-K + \sqrt{K^2 + 4Kc}}{2c} \quad (7)$$

<sup>1</sup> *Z. physik. Chem.*, **2**, 36 (1888).

When  $K^2$  and  $K$  are small in comparison with  $\sqrt{K}$ , as is true of weak electrolytes, the approximation

$$\alpha = \sqrt{\frac{K}{c}} \quad (8)$$

usually suffices.

When the degree of dissociation of an electrolyte is 0.5, then

$$K = \frac{(0.5)^2 c}{(1 - 0.5)} = 0.5c$$

Accordingly, the dissociation constant of an electrolyte represents one-half that concentration at which the electrolyte is 50 per cent dissociated. For example, since the dissociation constant of acetic acid is 0.000018 at 18°, one-half of this acid exists in the form of ions in a 0.000036 normal solution. It is evident that  $\sqrt{K}$  represents the ionic concentration in a normal solution of an electrolyte for which equation 8 holds.

On substituting  $\Lambda/\Lambda_0$  for  $\alpha$  in equation 5, we obtain the expression

$$\frac{\Lambda^2 c}{\Lambda_0(\Lambda_0 - \Lambda)} = K \quad (9)$$

by means of which the dissociation constant may be calculated directly from conductance data. This equation also gives the trend of the equivalent conductance with concentration.

**Experimental Proof of the Dilution Law.** The dilution law was first verified experimentally by Ostwald,<sup>1</sup> and later it was thoroughly tested by van't Hoff and Reicher.<sup>2</sup> How completely the results of these investigators substantiate the validity of the law for weak electrolytes is shown by the data in Table LXXVII.

Further evidence of the validity of the dilution law for weak electrolytes is to be found in the fact that values of the dissociation constant, calculated from conductance data, are constant over a large range of concentrations.<sup>3</sup> This constancy is illustrated by Bredig's data<sup>4</sup> for ammonium hydroxide and methylamine at 25°, in Table LXXVIII.

The requirements of the law of mass action are satisfied much more closely by the experimental data for the dissociation of weak electrolytes in aqueous solution than by the corresponding data for thermal dissociation in any gaseous system which has hitherto been subjected to exact

<sup>1</sup> *Ibid.*, 2, 36, 270 (1888).

<sup>2</sup> *Ibid.*, 2, 777 (1888).

<sup>3</sup> Cf. Ostwald, *Z. physik. Chem.*, 3, 170, 241, 369 (1889).

<sup>4</sup> *Ibid.*, 13, 289 (1894).

TABLE LXXXVII

EXPERIMENTAL VERIFICATION OF THE DILUTION LAW

Dilution $V = \frac{1}{c}$	$\Delta$	100 $\alpha$ Observed	100 $\alpha$ Calculated
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## Acetic Acid at 19.1°

$\Delta_0 = 335$		$K = 2.17 \times 10^{-5}$	
9.269	4.69	1.4	1.49
$9.269 \times 2$	6.69	2	1.99
$9.269 \times 2^2$	9.38	2.8	2.8
$9.269 \times 2^3$	13.2	3.94	3.93
$9.269 \times 2^4$	18.6	5.54	5.52
$9.269 \times 2^5$	25.9	7.75	7.71
$9.269 \times 2^6$	35.9	10.7	10.7
$9.269 \times 2^7$	49.6	14.8	14.8
$9.269 \times 2^{10}$	122	36.3	36.2

## Butyric Acid at 19.1°

$\Delta_0 = 327$		$K = 1.88 \times 10^{-5}$	
5.6	3.23	0.99	1.03
$5.6 \times 2$	4.69	1.43	1.44
$5.6 \times 2^2$	6.69	2.04	2.03
$5.6 \times 2^3$	9.44	2.88	2.86
$5.6 \times 2^4$	13.2	4.04	4.02
$5.6 \times 2^6$	25.8	7.88	7.88
$5.6 \times 2^8$	49.4	15.1	15.1

## Benzoic Acid at 19.1°

$\Delta_0 = 307$		$K = 8.36 \times 10^{-5}$	
43.89	18	5.85	5.87
$43.89 \times 2$	25.1	8.19	8.2
$43.89 \times 2^2$	35	11.4	11.4
$43.89 \times 2^3$	48.4	15.7	15.7
$43.89 \times 2^4$	65.9	21.5	21.4
$43.89 \times 2^5$	88.6	28.9	29
$43.89 \times 2^6$	117	38.1	38.1

measurement. This point was emphasized by Partington,<sup>1</sup> who pointed out that the dilution law comes out of such a comparison with flying colors. At high concentrations, however, the law ceases to hold; Wegscheider<sup>2</sup> concluded that it is strictly valid only above dilutions of 16 to 32 liters, but Partington<sup>1</sup> places the limiting dilution at 5 liters.

TABLE LXXVIII  
EXPERIMENTAL VERIFICATION OF THE DILUTION LAW

V	Ammonium Hydroxide $\Lambda_0 = 237$		Methylamine $\Lambda_0 = 225$	
	$\Lambda$	$K \times 10^5$	$\Lambda$	$K \times 10^5$
8	3.20	2.3	14.1	52
16	4.45	2.3	19.6	52
32	6.28	2.3	27.0	51
64	8.90	2.3	36.7	50
128	12.63	2.3	49.4	49
256	17.88	2.4	65.4	47

**The Influence of Temperature and Pressure on the Dissociation of Electrolytes.** It is well known that the equilibrium of any system is disturbed by a change in any of the factors of equilibrium, such as temperature or pressure. The manner in which the equilibrium of a system is displaced by changes in these factors is described by the principle formulated by Le Châtelier, which states: when any system is in a state of chemical or physical equilibrium, every change in one of the factors of equilibrium occasions a rearrangement of the system in such a direction that the factor in question experiences a change in a sense opposite to the original change. The influence of temperature on electrolytic dissociation follows from Le Châtelier's principle. Thus, if the temperature of a solution of an electrolyte is increased, a displacement of the equilibrium between the ions and the undissociated molecules will occur in that direction which is attended with the absorption of heat. Accordingly, the degree of dissociation of an electrolyte will decrease on a rise in temperature if the process of dissociation is exothermic; if the process is endothermic, the degree of dissociation will increase.

<sup>1</sup> *Trans. Faraday Soc.*, **15**, 98 (1919).

<sup>2</sup> *Z. physik. Chem.*, **69**, 611 (1909).

From a study of the results obtained in accurate determinations of the dissociation constants in aqueous solution of formic,<sup>1</sup> acetic,<sup>2</sup> propionic,<sup>3</sup> and chloroacetic<sup>4</sup> acids, as well as of other electrolytes, Harned and Embree<sup>5</sup> have observed that the dissociation constants of these electrolytes first increase, then pass through a maximum, and finally decrease with increasing temperature. If  $\log K$  is plotted against the Centigrade temperature ( $t$ ), it is found that the resulting curves are superimposable. Hence, when  $(\log K - \log K_m)$  is plotted against  $(t - \theta)$ , all points representing this function fall on the same curve. Here  $K_m$  is the maximum value of the dissociation constant and  $\theta$  is the temperature corresponding to this value. The following values of  $\theta$  have been determined:  $\text{HSO}_4^-$ ,  $-27.6$ ; chloroacetic acid,  $-5.4$ ; propionic acid,  $20.9$ ; acetic acid,  $22.6$ ; formic acid,  $24.7$ ;  $\text{H}_2\text{PO}_4^-$ ,  $43.1$ .

TABLE LXXIX  
THE PRESSURE COEFFICIENT OF DISSOCIATION

Pressure kg per sq cm	Pressure Coefficient at:	
	19.18°	40.00°
1	0.000	0.000
500	0.105	0.113
1000	0.187	0.199
1500	0.252	0.270
2000	0.301	0.321
2500	0.339	0.365
3000	0.365	0.396

In view of the foregoing, it is evident that, in any comparison of dissociation constants in relation to chemical structure (see Chapter XVI), values of dissociation constants at the corresponding temperatures  $\theta$  should be employed.

At the suggestion of Arrhenius, Fanjung<sup>6</sup> investigated the influence of pressure—up to 260 atmospheres—on electrolytic dissociation. He

<sup>1</sup> Harned and Embree, *J. Am. Chem. Soc.*, **56**, 1042 (1934).

<sup>2</sup> Harned and Ehlers, *ibid.*, **54**, 1350 (1932).

<sup>3</sup> Harned and Ehlers, *ibid.*, **55**, 652 (1933); cf. also Harned and Robinson, *Trans. Faraday Soc.*, **36**, 973 (1940).

<sup>4</sup> Wright, *J. Am. Chem. Soc.*, **56**, 314 (1934).

<sup>5</sup> *Ibid.*, **56**, 1050 (1934).

<sup>6</sup> *Z. physik. Chem.*, **14**, 673 (1894).

found that at the highest pressures the conductance exhibited an increase of about 9 per cent. Later, Körber<sup>1</sup> studied the influence of pressure on the degree of dissociation of acetic acid, using pressures up to 3000 kilograms per square centimeter. This investigator observed that the degree of dissociation of the acid increased as the pressure was raised. In Table LXXIX are given some of the values obtained for the pressure coefficient of the degree of dissociation  $\left(\frac{1}{\alpha} \cdot \frac{d\alpha}{dp}\right)$  of acetic acid at 19.18°

and 40.00°. It will be observed from the values in the table that the relative change in the dissociation of acetic acid, due to increase in pressure, increases with temperature.

**Dilution Formulas for Strong Electrolytes.** Although the validity of the dilution law for aqueous solutions of a very large number of weak electrolytes, especially the organic acids and bases, has been substantiated by the results of numerous investigations covering a period of more than fifty years, it appears to fail entirely when applied to aqueous solutions of strong binary electrolytes, as was first pointed out by van't Hoff and Planck, and to many non-aqueous solutions.<sup>2</sup> With non-aqueous solutions, the deviations from the simple law of mass action are often more pronounced than with aqueous solutions. Except in extremely dilute solutions, the value of the dissociation constant of most strong electrolytes varies considerably with concentration, whether it is calculated from degrees of dissociation obtained by either the freezing-point or the conductance method. It has been found that apparently the law breaks down in two directions: (1) if the ionic concentration of the solution is large, and (2) if the total—i.e., ionic plus molecular—concentration is large.

Owing to the failure of the dilution law for strong electrolytes, various empirical formula<sup>3</sup> were proposed, from time to time, to represent the variation of conductance with concentration. Most of these attempts to satisfy experimental data have no theoretical significance, and consist in altering indices or in adding terms to the dilution law. The equation proposed by Rudolph<sup>4</sup> differs from the dilution law in that  $\sqrt{c}$  is substituted for  $c$ . This expression has the form

$$k = \frac{\alpha^2 \sqrt{c}}{(1 - \alpha)} \quad (10)$$

<sup>1</sup> *Z. physik. Chem.*, **67**, 212 (1909).

<sup>2</sup> A very comprehensive review of this subject has been published by Ebert, *Jahrb. Radioakt. Elektronik*, **18**, 134 (1921).

<sup>3</sup> For a survey of the literature on the dilution law and dilution formulas, see Partington, *J. Chem. Soc.*, **97**, 1158 (1910); *Trans. Faraday Soc.*, **15**, 98 (1919).

<sup>4</sup> *Z. physik. Chem.*, **17**, 385 (1895).

where  $k$  is a constant. In this and the following formulas,  $\alpha$  is written for  $\Lambda/\Lambda_0$ . Van't Hoff <sup>1</sup> showed that somewhat more constant values for  $k$  are given by the expression :

$$k = \frac{(\alpha c)^3}{[(1 - \alpha)c]^2}$$

or

$$k = \frac{\alpha^{3/2} \sqrt{c}}{(1 - \alpha)} \quad (11)$$

In Table LXXX are given values of  $k$ , calculated by means of equation 11, for a number of strong electrolytes.

TABLE LXXX

$c$	KCl	KClO <sub>3</sub>	KNO <sub>3</sub>	NaCl	NH <sub>4</sub> Cl
0.1	1.81	1.27	1.7	1.55	1.68
0.05	1.71	1.28	1.52	1.44	1.66
0.01	1.68	1.26	1.48	1.44	1.52
0.005	1.63	1.11	1.48	1.52	1.48
0.001	1.56	1.05	1.5	1.63	1.49

Equation 11 was modified by Storch <sup>2</sup> to read

$$k = \frac{(\alpha c)^n}{(1 - \alpha)c} \quad (12)$$

where  $n$  is a constant the value of which varies slightly from 1.5 with the nature of the electrolyte. For aqueous solutions of strong electrolytes, this equation has been found to represent remarkably well the change in conductance with concentration, even up to high concentrations. The results obtained with the dilution law and equations 10, 11, and 12, with aqueous solutions of trimethyl-para-tolylammonium iodide, are compared in Table LXXXI.<sup>3</sup>

Later, Arrhenius <sup>4</sup> put equation 12 in the more general form :

$$k = \frac{\alpha^2 c}{(1 - \alpha)} \cdot (\alpha c)^{n-2} \quad (13)$$

or

$$f = \frac{\alpha^2 c}{(1 - \alpha)} = k(\alpha c)^m \quad (14)$$

<sup>1</sup> *Z. physik. Chem.*, **18**, 300 (1895).

<sup>2</sup> *Ibid.*, **19**, 13 (1896).

<sup>3</sup> Creighton and Way, *J. Franklin Inst.*, **186**, 675 (1918).

<sup>4</sup> *Z. physik. Chem.*, **31**, 197 (1899).

where  $m = 2 - n$ , and  $f$  is the mass-action function. Arrhenius showed that this equation holds over a wide range of concentrations, not only for solutions of single electrolytes, but also for solutions of mixtures of salts. It is evident, however, that the application of equation 14 cannot be general, since it does not reduce to the dilution law at low concentrations.

TABLE LXXXI  
COMPARISON OF DILUTION FORMULAS

$V$	$\alpha$	$K = \frac{\alpha^2 c}{(1 - \alpha)}$	$k_1 = \frac{\alpha^2 \sqrt{c}}{(1 - \alpha)}$	$k_2 = \frac{\alpha^{3/2} \sqrt{c}}{(1 - \alpha)}$	$k_3 = \frac{(\alpha c)^n}{(1 - \alpha)c}$ $n = 1.40$
29.31	0.809	0.117	0.633	0.495	1.01
58.62	0.851	0.083	0.635	0.473	1.07
117.24	0.884	0.058	0.622	0.438	1.08
234.48	0.909	0.039	0.593	0.387	1.08
468.96	0.926	0.025	0.535	0.309	1.04
937.92	0.941	0.016	0.490	0.255	1.01
1875.84	0.955	0.011	0.468	0.229	1.02
				Mean:	1.04

On account of the very wide applicability of equation 14, Kraus<sup>1</sup> was led to combine it with equation 5, obtaining the expression

$$f = \frac{\alpha^2 c}{(1 - \alpha)} = K + k(\alpha c)^m \quad (15)$$

where  $K$  is the mass-action constant, and the other quantities have their previous significance. This expression is known as the Kraus and Bray dilution formula. Since the second term of the right-hand member of equation 15 decreases with concentration, the expression reduces to the dilution law at low concentrations. At high concentrations, where the first term of the right-hand member becomes small in comparison with the second term, the expression approaches equation 14 as a limit. The equation shows that, when  $m$  is less than unity, the equivalent conductance increases continuously with decreasing concentration, whereas, when  $m$  is greater than unity, the conductance passes through a minimum.

Kraus and Bray<sup>2</sup> showed that equation 15 is applicable to solutions of a large number of strong electrolytes in 26 non-aqueous solvents over a wide concentration range. With aqueous solutions, however, the equation does not give such good results. The fact that, in general,  $\Lambda/c^n$  is

<sup>1</sup> *Proc. Am. Chem. Soc.*, **1909**, 15; cf. also Bray, *Trans. Am. Electrochem. Soc.*, **21**, 143 (1912); Kraus and Bray, *J. Am. Chem. Soc.*, **35**, 1315 (1913).

<sup>2</sup> *J. Am. Chem. Soc.*, **35**, 1315 (1913).



constant<sup>1</sup> tends to confirm the validity of equation 15, since this is the form to which it reduces by approximation at the concentrations investigated.

According to the Kraus and Bray dilution formula, the mass-action function,  $f = (\alpha^2 c)/(1 - \alpha)$ , is a linear function of the ionic concentration raised to the  $m$ th power. Hence, if values of  $f$  are plotted against

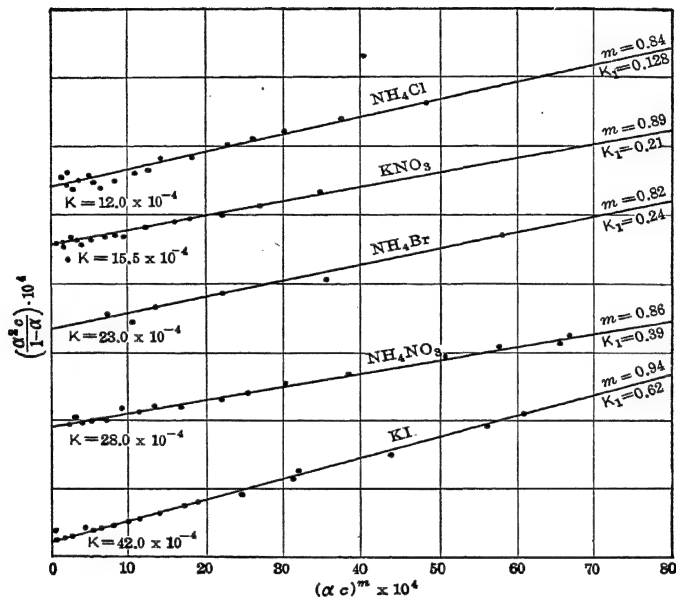


FIG. 82.

the corresponding values of  $(\alpha c)^m$ , the points obtained should lie on a straight line if the formula holds. Curves obtained in this way for solutions of a number of electrolytes in liquid ammonia are given in Fig. 82.<sup>2</sup> The value of the true mass-action constant  $K$  is given by the intercept on the  $f$ -axis at  $(\alpha c)^m = 0$ ; that of the constant  $k$  is given by the slope of the line. The value of the constant  $m$  may be obtained by plotting  $\log(f - K)$  against  $\log(\alpha c)$ , an arbitrary value being chosen for  $K$ .

In accordance with equation 15, any deviation from the dilution law is solely a function of the ionic concentration, a conclusion that is not in harmony with certain experimental results. Many organic acids obey

<sup>1</sup> Sachanov and Prscheborovski, *Z. Elektrochem.*, **20**, 39 (1914).

<sup>2</sup> Kraus and Bray, *loc. cit.*, p. 1333.

the dilution law at ionic concentrations several hundred times greater than those at which salts begin to show considerable deviations. Further, Holmberg<sup>1</sup> found that the law of mass action is strictly applicable to the dissociation of the iodides of sodium and potassium at concentrations from 0.05 to 1.0 normal; and Schlesinger and Coleman<sup>2</sup> showed that, although the alkali formates are largely dissociated in anhydrous formic acid, these solutions obey the dilution law with a high degree of accuracy. On the other hand, the dilution law does not hold for certain weak electrolytes. From these and similar results, it would appear that the failure of the dilution law cannot be attributed solely to a high ionic concentration.<sup>3</sup>

**Explanations of the Anomaly of Strong Electrolytes.** The anomaly of strong electrolytes was long regarded as the *bête noire* of the classical theory of electrolytic dissociation. As might have been expected, the deviations of solutions of strong electrolytes from the dilution law were the subject of a great deal of controversy, and numerous explanations were suggested to account for the anomaly. Among the various causes to which the deviations were attributed, the following may be mentioned: (1) the use of incorrect values for the degree of dissociation; (2) incorrect representation of the dissociation equilibrium by the equation  $MA \rightleftharpoons M^+ + A^-$ ; (3) changes in the dissociating power of the solvent; and (4) dissociation of the solvent with increasing concentration.

It was early recognized that values of the degree of dissociation derived from conductance measurements might be incorrect. Since variations in the equivalent conductance with concentration may arise from change either in the number or in the mobilities of the ions, the degree of dissociation is correctly given by the conductance ratio  $\Lambda/\Lambda_0$  only if the ionic mobilities are constant. There is reason to believe that this is not even approximately true for strong electrolytes. Changes in mobility with concentration may arise from variations in ionic friction or in inter-ionic forces. On the other hand, degrees of dissociation obtained by freezing-point measurements may be erroneous, owing to causes of a physical or chemical nature. For example, forces may operate in solution which alter, more or less, the number of independent particles; or the concentration of the particles may be changed by the formation of complexes (inner complexes), through the union of ions and undissociated molecules.<sup>4</sup>

<sup>1</sup> *Svensk. Kem. Tidskr.*, **1918**, 6.

<sup>2</sup> *J. Am. Chem. Soc.*, **38**, 271 (1916).

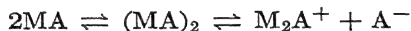
<sup>3</sup> Cf. Neale, *Trans. Faraday Soc.*, **17**, 505 (1922).

<sup>4</sup> Cf. Bredig, *Z. physik. Chem.*, **13**, 262 (1894); Noyes, *ibid.*, **36**, 63 (1901); Biltz, *ibid.*, **40**, 185 (1902); Steele, *ibid.*, **40**, 722 (1902); Donnan, Bassett, and Fox, *J. Chem. Soc.*, **81**, 944 (1902).

It is obvious that the dilution law can be expected to hold for binary electrolytes only when the dissociation equilibrium—for a uniunivalent electrolyte—is expressed by the equation



If, for example, a uniunivalent electrolyte dissociated in accordance with the equation



the dilution law would not express the change in dissociation with concentration. If the solvent takes part in the process of dissociation, as has been suggested (see Chapter IV), the dilution law must fail, because in such an event the concentration of the solvent must be contained in the mass-action expression. On the assumption that dissociation is brought about by collision of the solute molecules with the solvent molecules, Kendall<sup>1</sup> wrote the mass-action law in the form

$$\frac{C_i^2}{C_u \cdot C_s} = k \quad (16)$$

where  $C_i$ ,  $C_u$ , and  $C_s$  are the concentrations of the ions, the undissociated molecules, and the solvent molecules, respectively.

The hypothesis that the dissociating power of the solvent increases with the concentration of the solute<sup>2</sup> appears to be invalidated by the fact that experimental evidence fails, in general, to indicate an increase in the dissociation constants of weak acids or bases caused by neutral salts, as shown by McBain and Coleman.<sup>3</sup> By means of "complete migration measurements" (i.e., measurements in which all the constituents of the solution, without exception, are determined after electrolysis) in solutions of different concentrations, these investigators found<sup>4</sup> that the sum of the movements of the ions of the electrolyte was equal to the total current passed through the solution. This result is not in harmony with the suggestion<sup>5</sup> that the failure of the dilution law is attributable to an increase in the dissociation of the solvent sufficient to affect appreciably the conductance of the solution; or, indeed, that the solvent conducts at all.

The problem of the behavior of strong electrolytes will be discussed further in Chapter XV.

<sup>1</sup> *J. Am. Chem. Soc.*, **36**, 1069 (1914).

<sup>2</sup> Cf. Walden, *ibid.*, **35**, 1649 (1913).

<sup>3</sup> *J. Chem. Soc.*, **105**, 1517 (1914).

<sup>4</sup> *Trans. Faraday Soc.*, **15**, 27 (1919).

<sup>5</sup> LeBlanc, *Z. physik. Chem.*, **8**, 314 (1891); Noyes, *ibid.*, **9**, 614 (1892); Walden, *J. Am. Chem. Soc.*, **35**, 1649 (1913).

**Summary.** It has been shown that the law of mass action, in the form of Ostwald's dilution law, expresses correctly the dissociation equilibrium in aqueous solutions of weak binary electrolytes. With aqueous solutions of strong electrolytes of this type, as well as with many non-aqueous solutions, the law appears to fail entirely, except at very low concentrations. Various formulas, many of which approach the dilution law as a limiting form, have been proposed to represent the variation of the conductance of solutions of strong electrolytes with concentration. Most of these expressions have no theoretical significance, and all are limited in their application.

#### REFERENCE

KRAUS, *The Properties of Electrically Conducting Systems*, Chapters IV and XII, 1922.

#### PROBLEMS

1. Given that the dissociation constants of adipic acid, citraconic acid, malic acid, benzoic acid, and succinic acid at  $25^{\circ}$  are, respectively,  $3.7 \times 10^{-5}$ ,  $3.4 \times 10^{-5}$ ,  $3.95 \times 10^{-4}$ ,  $6.6 \times 10^{-5}$ , and  $6.8 \times 10^{-5}$ , calculate the concentrations at which these acids are 50 per cent dissociated at this temperature.

2. Ostwald found that, at  $25^{\circ}$ , at dilutions of 64, 128, 256, 512, and 1024 liters, the equivalent conductance of butyric acid was 10.86, 15.27, 21.33, 29.52, and 40.62 mhos, respectively, and at zero concentration, 356 mhos. From these data calculate the mean value of the dissociation constant of the acid at  $25^{\circ}$ .

3. At  $25^{\circ}$ , the equivalent conductance of a solution containing 1 equivalent of cyanacetic acid in 64 liters is 138.1, and at zero concentration it is 362. Calculate the dissociation constant of the acid at  $25^{\circ}$ .

4. At  $25^{\circ}$ , the equivalent conductance of a solution containing 1 equivalent of monobromacetic acid in 32 liters is 68.7 mhos, and at infinite dilution it is 322. Calculate the dissociation constant of the acid.

5. The specific conductance of a 0.0625 normal solution of acrylic acid is 0.0006625 mho at  $25^{\circ}$ , and that of a 0.00098 normal solution of sodium acrylate is 0.000851. Given that the salt is completely dissociated at the above concentration, and that the conductances of the hydrogen and sodium ions at  $25^{\circ}$  are 347 and 51.2 respectively, calculate the dissociation constant of the acid.

6. At  $18^{\circ}$ , the specific conductance of acetic acid at a dilution of 512 liters is 0.000629 mho. The conductances of the hydrogen and acetate ions at  $18^{\circ}$  are 313 and 35, and their temperature coefficients are 0.0154 and 0.0238, respectively. Calculate the dissociation constant of the acid at  $25^{\circ}$ .

7. (Cf. preceding problem.) At what dilution is the concentration of the hydrogen ions in a solution of acetic acid, at  $25^{\circ}$ , 0.035 normal?

8. At  $25^{\circ}$  the dissociation constants of isobutyric and glycolic acids are  $1.44 \times 10^{-5}$  and  $1.52 \times 10^{-4}$ , respectively. At what dilution has a solution of isobutyric acid the same hydrogen-ion concentration as a 0.01 normal solution of glycolic acid?

9. (Cf. preceding problem.) What is the ratio of the hydrogen-ion concentrations in solutions of isobutyric and glycolic acids at equal dilutions?

## CHAPTER XIV

### THE ACTIVITY OF STRONG ELECTROLYTES

**Fugacity.** As we have already seen in Chapter III, the relation between the vapor pressure ( $p_1$ ) of a pure solvent and that ( $p'_1$ ) of the solvent in a solution containing  $n_2$  moles of a solute and  $n_1$  moles of the solvent is expressed by Raoult's law

$$\frac{p_1 - p'_1}{p_1} = \frac{n_2}{n_1 + n_2}$$

or

$$p'_1 = p_1 \frac{n_1}{n_1 + n_2} = p_1 N_1 \quad (1)$$

where  $N_1$  is the mole fraction of the solvent in the solution. This law, though sufficiently accurate for many purposes, is obeyed *exactly* only when the vapor pressure constitutes a true measure of the tendency of a molecular species to escape from its surroundings as a *perfect* gas. Actually, this occurs only when the concentration of the solution is zero, i.e., when the solution is *ideal*. Indeed, an ideal solution might be defined as one which exactly obeyed Raoult's law.

Closely related to the vapor pressure is a quantity which is called **fugacity**,  $\xi$ , introduced by G. N. Lewis.<sup>1</sup> According to him, "the fugacity bears to the vapor pressure a relation analogous to the relation between a perfect gas thermometer and a thermometer filled with some actual gas. The fugacity will be equal to the vapor pressure when the vapor is a perfect gas, and in general may be regarded as an 'ideal' or 'corrected' vapor pressure." Since, then, fugacity is vapor pressure corrected for its deviations from the simple gas laws, it would be preferable to express Raoult's law in terms of fugacities when accuracy is sought. Accordingly, equation 1 may be written in the form

$$\xi'_1 = \xi_1 N_1 \quad (2)$$

where  $\xi_1$  and  $\xi'_1$  are the fugacities of the solvent in the pure state and in the solution.

<sup>1</sup> *Proc. Am. Acad. Arts Sci.*, **37**, 49 (1901); *Z. physik. Chem.*, **38**, 205 (1901).

**The Activity Concept.** Although the individual fugacities are usually unknown, the relative fugacity

$$\frac{\xi'}{\xi} = a \quad (3)$$

can often be calculated.<sup>1</sup> This ratio of the fugacity  $\xi'$  of a molecular species in some given state to its fugacity  $\xi$  in a chosen *standard state* is called the **activity** of the species, and is denoted by the symbol  $a$ . For a solution containing  $n_1$  moles of solvent and  $n_2$  moles of solute, the activities of the solvent and solute are, respectively:

$$\frac{\xi'_1}{\xi_1} = a_1 \quad \frac{\xi'_2}{\xi_2} = a_2 \quad (4)$$

The activity  $a$  represents the *effective* concentration of a molecular species and replaces Guldberg and Waage's vague concept of "active mass." The foregoing definition of activity is independent of whether the solution is ideal or not. If, however, the solution is ideal, then the activities of the components are identical with their mole fractions; e.g.,

$$a_1 = N_1 \quad a_2 = N_2 \quad (5)$$

The concept of activity has been used very extensively in the study of strong electrolytes, and its utility has been fully justified.

**The Activity of Ions.** When the ratio of the effective ion concentrations  $C_2/C_1$  of two solutions of an electrolyte is calculated from the electromotive force of a concentration cell, by means of equation 2, Chapter IX, the value obtained does not agree with that derived from the equation

$$\frac{\Lambda_c \eta_c}{\Lambda_0 \eta_0} = \alpha$$

That is,  $C_2/C_1$  is not equal to  $\alpha_2 c_2 / \alpha_1 c_1$ , where  $c$  is the concentration of the electrolyte. This disagreement is illustrated by the data<sup>2</sup> given in Table LXXXII for potassium chloride at 25°.

It will be observed that the values of  $C_2/C_1$  are always less than those of  $\alpha_2 c_2 / \alpha_1 c_1$ . The ratio of the effective ion concentrations, which is equal to the ratio of the activities of the ions in the two solutions of the electrolyte, i.e.,  $C_2/C_1 = a_2/a_1$ , is called the **activity ratio**.

The activities of the cation and anion of a strong binary electrolyte, MA, may be represented by  $a_+$  and  $a_-$ , respectively. Denoting the

<sup>1</sup> For various methods for the numerical calculations, the reader is referred to Lewis and Randall's *Thermodynamics*, pp. 259-267, 1923.

<sup>2</sup> MacInnes and Parker, *J. Am. Chem. Soc.*, **37**, 1445 (1915).

TABLE LXXXII

COMPARISON OF IONIC CONCENTRATIONS DERIVED FROM CONDUCTANCE AND ELECTROMOTIVE FORCE MEASUREMENTS

Concentration Ratio $c_2 : c_1$	$\frac{\alpha_2 c_2}{\alpha_1 c_1}$ (Conductance)	$\frac{C_2}{C_1}$ (emf)
0.5 : 0.05	8.85	8.09
0.1 : 0.01	9.16	8.33
0.05 : 0.005	9.30	8.64
0.01 : 0.001	9.62	9.04

activity of the undissociated solute by  $a_2$ , the equilibrium between these molecular species is given by the law of mass action

$$\frac{a_+ a_-}{a_2} = K \quad (6)$$

This expression is strictly valid, and  $K$  is accordingly an exact constant. (It will be recalled that Ostwald's dilution law does not hold even approximately for strong electrolytes.) Indeed, the law of mass action is universally valid when expressed in terms of activities or fugacities. Hence, it might be stated that the activities of molecular species are those quantities which, when substituted for concentrations in the mass-action equation, express their effect in determining the equilibrium of these species.

The ion activities  $a_+$  and  $a_-$  can be determined by several methods, e.g., by the electromotive force method referred to above. If the electrolyte is volatile, like the halogen hydrides, the activity of the undissociated molecules  $a_2$  is proportional to the vapor pressure of the electrolyte. Unfortunately, this method of determining the activity of the undissociated molecules has but very limited application, owing to the fact that strong electrolytes usually have an inappreciable vapor pressure. Accordingly, it has been found convenient to define the activity of the undissociated molecules of the electrolyte by putting  $K$  in equation 6 equal to unity and writing

$$a_+ a_- = a_2 \quad (7)$$

It follows from this that, at zero concentration, when the solution becomes ideal,

$$a_+ = a_- = c = a_2^{1/2} \quad (8)$$

where  $c$  is the molal concentration of the solute. Because it is not certain how far this equality of the activities of the cation and anion extends into

the range of finite concentrations, it is customary to consider the mean activity of the ions. This quantity is denoted by the symbol,  $a_{\pm}$ , and is defined as the geometrical mean of the activities of the two kinds of ions. Hence

$$a_{\pm} = (a_+ a_-)^{1/2} = a_2^{1/2} \quad (9)$$

**The Activity Coefficient.** It will be recalled that in the derivation of equation 14, Chapter V, for the degree of dissociation of a binary electrolyte, it was assumed that: (1) the conductance of an electrolyte depends upon the concentrations of the ions and upon their respective mobilities,  $u$  and  $v$ ; and (2) the mobilities are independent of the concentration of the electrolyte. However, the mobilities of ions *do* vary with concentration.<sup>1</sup> Moreover, it has been shown in the preceding chapter that the degree of dissociation of strong electrolytes is not in agreement with the law of mass action. In consequence of these and other difficulties (e.g., the hypothesis of complete dissociation of strong electrolytes, which will be discussed in the following chapter), the significance of the degree of dissociation, as determined by the conductance ratio, has been seriously questioned, and, in the interpretation of the properties of strong electrolytes, it has been almost universally replaced by the **activity coefficient** or the **thermodynamic degree of dissociation**. The activity coefficient is defined as the ratio of the mean activity of the ions,  $a_{\pm}$ , to the total molal concentration ( $c$ ) of the electrolyte, and is represented by the symbol  $\gamma$ . Accordingly, for a binary electrolyte,

$$\gamma = \frac{a_{\pm}}{c} \quad (10)$$

The expression for the activity coefficient of a strong electrolyte yielding more than two ions may be obtained as follows: Let us consider, for example, the dissociation of a univalent electrolyte,  $M_2A$ :



If the stoichiometrical molal concentration,  $c$ , is very small,  $a_+ = 2c$ ,  $a_- = c$ , and  $a_{\pm} = (2c^2 \times c)^{1/3} = c\sqrt[3]{4}$ . Since at zero concentration the activity coefficient must be equal to unity, it follows that  $\gamma = a_{\pm}/c\sqrt[3]{4}$ . In general, if  $\nu_+$  and  $\nu_-$  are the numbers of ions produced by the dissociation of one mole of electrolyte:

$$\gamma = \frac{a_{\pm}}{c(\nu_+^{\nu_+} \times \nu_-^{\nu_-})^{1/\nu}} \quad (11)$$

where  $\nu = \nu_+ + \nu_-$ .

<sup>1</sup> Lewis, *J. Am. Chem. Soc.*, **34**, 1631 (1912).



If the stoichiometrical molal concentrations of the cation and anion of an electrolyte which yields two kinds of ions are represented by  $c_+$  and  $c_-$ , the activity coefficient of the former ion is  $\gamma_+ = a_+/c_+$  and that of the latter ion is  $\gamma_- = a_-/c_-$ . The activity coefficient of the electrolyte, sometimes called the mean activity coefficient, is  $\gamma = (\gamma_+\gamma_-)^{1/2}$ . In general, if a mole of an electrolyte is capable of furnishing  $\nu_+$  moles of cation and  $\nu_-$  moles of anion,

$$\gamma = (\gamma_+^{\nu_+} \gamma_-^{\nu_-})^{1/\nu} = \frac{a_{\pm}}{c_{\pm}} \quad (12)$$

where the mean molal concentration,  $c_{\pm}$ , is defined by the expression:

$$c_{\pm} = c(\nu_+^{\nu_+} \nu_-^{\nu_-})^{1/\nu} \quad (13)$$

Evidently, at zero concentration the activity coefficient of all ions is unity.<sup>1</sup>

From the results given in Table LXXXII, it is apparent that the activity coefficient and the degree of dissociation of potassium chloride are not identical at the concentrations employed. As indicated by the data in this table, the values of the activity coefficient and the degree of dissociation approach one another as the concentration decreases, and both become unity at zero concentration. If, therefore, it is assumed that these two quantities are equal at very low concentrations, values of the activity coefficient can be calculated at higher concentrations from electromotive-force measurements. The first measurements of this kind were made by Tolman and Ferguson<sup>2</sup> with hydrochloric acid. That the foregoing assumption is justified only at very low concentrations is shown by the data given in Table LXXXIII for potassium chloride at 25°. The activity coefficients given in the third column of the table were determined by Noyes and MacInnes<sup>3</sup> from electromotive-force measurements; those in the last column were calculated by Lewis and Linhart<sup>4</sup> from the results of freezing-point measurements. This table shows, for example, that the effective concentration of the potassium ion in 0.1 normal solution is 0.0745, while the concentration of this ion, when calculated from the degree of dissociation, is 0.0861. As differences such as this are too great to be attributed to experimental

<sup>1</sup> For work on the activity coefficients of ions, the reader is referred to MacInnes, *J. Am. Chem. Soc.*, **41**, 1086 (1919); Brown and MacInnes, *ibid.*, **57**, 1356 (1935); MacInnes and Brown, *Chem. Revs.*, **18**, 335 (1936).

<sup>2</sup> *J. Am. Chem. Soc.*, **34**, 232 (1912).

<sup>3</sup> *Ibid.*, **42**, 239 (1920).

<sup>4</sup> *Ibid.*, **41**, 1952 (1919).

TABLE LXXXIII

COMPARISON OF THE DEGREE OF DISSOCIATION AND THE ACTIVITY COEFFICIENT OF KCl

Concentration <i>c</i>	Degree of Dissociation $\alpha = \frac{\Delta_c \eta_c}{\Delta_0 \eta_0}$	Activity Coefficient from Measurements of:	
		emf	Freezing Point
0.00005	0.995	.....	0.995
0.0001	0.993	.....	0.993
0.0005	0.985	.....	0.984
0.001	0.979	(0.979)	0.977
0.005	0.956	0.923	0.946
0.01	0.941	0.890	
0.05	0.889	0.790	
0.1	0.861	0.745	

error, evidently some modification in the theory of electrolytic dissociation is required to explain the discrepancies.

In addition to electromotive-force and freezing-point measurements, activity coefficients can be determined from vapor-pressure measurements and solubility measurements,<sup>1</sup> the last being essentially vapor-pressure measurements into a solvent instead of into a vacuum.

Values of the activity coefficients of a number of electrolytes at 25°

TABLE LXXXIV  
ACTIVITY COEFFICIENTS AT 25°

Concentration (Molal)	0.01	0.02	0.05	0.1	0.2	0.5	1.0	3.0
HCl	0.924	0.894	0.860	0.814	0.783	0.762	0.823	1.35
LiCl	0.922	0.892	0.843	0.804	0.774	0.754	0.776	1.20
NaCl	0.922	0.892	0.842	0.798	0.752	0.689	0.650	0.704
KCl	0.922	0.892	0.840	0.794	0.749	0.682	0.634	.....
KOH	0.92	0.89	0.84	0.80	0.75	0.73	0.75	.....
AgNO <sub>3</sub>	0.902	0.857	0.783	0.723	0.655	0.526	0.396	.....
H <sub>2</sub> SO <sub>4</sub>	0.617	0.519	0.397	0.313	0.244	0.178	0.150	0.170
CuSO <sub>4</sub>	0.404	0.320	0.216	0.158	0.110	0.067	.....	.....

<sup>1</sup> Brönsted and LaMer, *J. Am. Chem. Soc.*, **46**, 555 (1924). For a full discussion of methods for the determination of activity coefficients, the reader is referred to Lewis and Randall, *Thermodynamics*, 1923.

are given in Table LXXXIV. These values were compiled by Lewis and Randall.<sup>1</sup> It will be observed that, unlike the degree of dissociation, the activity coefficients of a number of the electrolytes pass through a minimum value at a concentration of approximately 0.5 normal. Harned<sup>2</sup> found that the activity coefficient of potassium chloride passes through a minimum at a concentration of about 2 normal.

**Mixed Electrolytes.** To facilitate the study of solutions containing two or more strong electrolytes, a new concept, the **ionic strength**,  $\mu$ , was introduced by Lewis and Randall.<sup>3</sup> The ionic strength of a solution is defined as one-half the sum of the stoichiometrical molal concentrations of all the ions present, each multiplied by the square of its valence or charge. Thus, the ionic strength of a solution is given by the expression

$$\mu = \frac{1}{2}(c_+z_+^2 + c_-z_-^2 + c'_+z'^2_+ + c'_-z'^2_- + \dots) \quad (14)$$

$$= \frac{\sum c_i z_i^2}{2} \quad (14a)$$

where  $c$  is the molal concentration and  $z$  is the valence of the ions. For example, the ionic strength of a solution which is 0.01 molal with respect to  $K_2SO_4$  and 0.02 molal with respect to  $MgCl_2$  is

$$\begin{aligned} \mu &= \frac{1}{2}(c_K z_K^2 + c_{SO_4} z_{SO_4}^2 + c_{Mg} z_{Mg}^2 + c_{Cl} z_{Cl}^2) \\ &= \frac{1}{2}(0.02 \times 1 + 0.01 \times 2^2 + 0.02 \times 2^2 + 0.04 \times 1) = 0.09 \end{aligned}$$

In our discussion of the activity coefficient, so far, we have considered only solutions of single strong electrolytes. In a solution containing two or more electrolytes, it might be expected that the activity coefficient of one of the electrolytes would be changed by the presence of the others. "We might guess the activity-coefficient of a given electrolyte to depend simply upon the total concentration of electrolytes, or to depend upon the total equivalent concentration (which would be assuming that one molecule of a bivalent ion has the effect of two molecules of a univalent ion). Neither of these two guesses is correct, although the latter comes nearer the truth than the former."<sup>4</sup> In attempting to solve this problem, Lewis and Randall<sup>4</sup> found a remarkably simple and precise rule which permits the calculation of the activity coefficients in dilute solutions of mixed electrolytes. This rule, which is in exact agreement with

<sup>1</sup> *J. Am. Chem. Soc.*, **43**, 1112 (1921).

<sup>2</sup> *Ibid.*, **38**, 1989 (1916).

<sup>3</sup> *Ibid.*, **43**, 1140 (1921).

<sup>4</sup> Lewis and Randall, *J. Am. Chem. Soc.*, **43**, 1140 (1921).

a multiplicity of equilibria exists between neutral and charged molecule, of many different degrees of complexity. In more concentrated systems phenomena may intervene of an entirely different type. In the light of our present knowledge, it seems safe to predict that the solution of the problem of electrolytes will probably not be found through a mere extension of the limiting laws that hold only at very low concentrations."

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### PROBLEMS

1. Using the necessary data given in Tables LXXXVI and LXXXVII, check the values in the latter table for the osmotic deviation of the solutions of potassium chloride, magnesium sulphate, and potassium sulphate.
2. Calculate the ionic strength of each of the solutions given in Table LXXXVII.

## CHAPTER XV

### THEORIES OF STRONG ELECTROLYTES

Apart from the evidence that the dilution law is valid for solutions, of sufficient dilution (i.e., 0.0001 normal), of all electrolytes, whether weak or strong,<sup>1</sup> its failure in application to solutions of strong electrolytes at even moderately low concentrations had to be recognized. This failure—according to Milner,<sup>2</sup> a failure so complete that insuperable obstacles stand in the path of the acceptance of any theory which attributes the change in conductance with concentration to variation in the number of ions—led a number of investigators<sup>3</sup> to reject the theory that strong electrolytes are dissociated to an extent depending upon the concentration, and to return to the hypothesis of complete dissociation in solution first put forward by Sutherland.<sup>4</sup>

**The Theory of Complete Dissociation.** By complete dissociation is meant that the dissolved solute consists wholly of electrically charged particles, but not necessarily particles which are free to move in an electric field as connoted by the older conception of ions. Indeed, the theory assumes that pairs of oppositely charged ions which are temporarily in close proximity may behave as though they were undissociated molecules. This theory ascribes the properties of strong electrolytes to the effects of interionic forces, effects which are neglected in the classical theory of Arrhenius.

Provided that dissociation were complete and each ion behaved independently of its neighbor, the osmotic pressure of a strong electrolyte would obey van't Hoff's ideal law, that is

$$P_c = \nu cRT \quad (1)$$

where  $\nu$  is the number of ions produced by the dissociation of one molecule of the electrolyte, and  $c$  is the molal concentration. The fact that

<sup>1</sup> Cf. Washburn, *J. Am. Chem. Soc.*, **40**, 150 (1918).

<sup>2</sup> *Phil. Mag.*, **35**, 214 (1918).

<sup>3</sup> Milner, *ibid.*, **23**, 551 (1912); **25**, 742 (1913); **35**, 214, 352 (1918); *Trans. Faraday Soc.*, **15**, 148 (1919); Bjerrum, *Z. Elektrochem.*, **24**, 321 (1918); Ghosh, *J. Chem. Soc.*, **113**, 449, 627, 707, 790 (1918); *Z. physik. Chem.*, **98**, 211 (1921); Debye and Hückel, *Physik. Z.*, **24**, 185, 304 (1923).

<sup>4</sup> *Phil. Mag.*, **3**, 161 (1902); **7**, 1 (1906).

the observed osmotic pressure ( $P_o$ ) of dilute solutions of strong electrolytes, except at extremely low concentrations, is invariably less than the ideal value ( $P_c$ ) is attributed, in the theory of complete dissociation, to the electric forces between the ions. The relation between the observed and the ideal osmotic pressure is given by the expression

$$P_o = f_o P_c \quad (2)$$

where  $f_o$ , the so-called **osmotic coefficient**,<sup>1</sup> is a fraction which increases as the concentration decreases and approaches unity at zero concentration. This coefficient, which is numerically equal to the mole number,  $i$ , divided by  $\nu$ , represents the effect of interionic forces on the osmotic pressure of the ions.

From the osmotic coefficient the **osmotic deviation** ( $\Theta$ ) may be obtained, for

$$\Theta = 1 - f_o = \frac{P_c - P_o}{P_c} \quad (3)$$

Since osmotic pressure and lowering of the freezing point are interdependent phenomena, the osmotic deviation may equally well be expressed in terms of the ideal ( $\Delta_c$ ) and the observed ( $\Delta_o$ ) lowering of the freezing point:

$$\Theta = 1 - f_o = \frac{\Delta_c - \Delta_o}{\Delta_c} \quad (4)$$

Similar considerations apply to the conductance of strong electrolytes.

Although no direct evidence has been found for the existence of either complete dissociation or undissociated molecules, the concept of complete dissociation has been generally accepted as a working hypothesis, variation with concentration of the conductance ratio,  $\Delta_c/\Delta_o$ , and other properties of solutions of electrolytes being attributed to changes in interionic forces. This simple hypothesis explains why so many dissimilar chemical compounds appear to be dissociated to the same extent (see Table XXII),<sup>2</sup> and why a volatile substance like hydrogen chloride does not have an appreciable vapor pressure even in normal solution where, according to the conductance ratio, 15 per cent of the acid is undissociated.<sup>3</sup> Among other points adduced in favor of the hypothesis of complete dissociation may be mentioned the *complete* extraction of silver perchlorate from benzene by water;<sup>4</sup> the agreement between the

<sup>1</sup> Cf. Bjerrum, *Z. Elektrochem.*, **24**, 321 (1918).

<sup>2</sup> Cf. Brönsted, *Medd. K. Vetenskapsakad. Nobelinst.*, **5**, No. 25, 1 (1919).

<sup>3</sup> Wynne-Jones, *J. Chem. Soc.*, **1930**, 1064, has estimated the concentration of undissociated molecules in normal hydrochloric acid to be  $4 \times 10^{-8}$ .

<sup>4</sup> Hill, *J. Am. Chem. Soc.*, **43**, 254 (1921).

mobilities of the chloride ion determined from various uniunivalent chlorides up to 0.1 normal;<sup>1</sup> the fact that in methyl and ethyl alcohol<sup>2</sup> and nitromethane<sup>3</sup> the change of the conductance of uniunivalent salts is of the same order as the change in viscosity; and the avoidance of improbable conclusions regarding the abnormal activity of undissociated molecules,<sup>4</sup> to which solubility effects lead when interpreted on the basis of older assumptions. Indeed, as Wolfenden<sup>5</sup> concludes, in "summarizing the evidence derived from the study of those properties believed to be characteristic of undissociated molecules, one may say, apart from acids, there is virtually no unequivocal evidence of the existence of molecules in solutions of 'strong' uniunivalent electrolytes at any concentration."

In supporting the theory of complete dissociation, Brönsted and LaMer<sup>6</sup> incline to the opinion that there are three distinct regions for dilute solutions of strong electrolytes: (1) a region of very low concentration where the simple gas laws are applicable within the limits of experimental error; (2) intermediate concentrations where the deviations from the gas laws depend only upon the valence type of the electrolyte, and (3) a region of higher concentration where the deviations are occasioned, in part, by the chemical nature and the size of the ions. In this ideal intermediate region, which is to be expected on the basis of the theory of complete dissociation, it was found<sup>7</sup> that the activity coefficient is expressed by the equation

$$-\ln \gamma = 3\beta\sqrt{c} \quad (5)$$

where  $\beta$  is a constant = 0.32 and  $c$  is the molal concentration. Since for this region the relation<sup>8</sup>

$$-\ln \gamma = 3(1 - f_o) \quad (6)$$

holds, it follows that

$$\Theta = \beta\sqrt{c} \quad (7)$$

For an electrolyte which yields ions of valence  $z_1$  and  $z_2$ , it was shown<sup>9</sup> that

<sup>1</sup> MacInnes and Cowperthwaite, *Trans. Faraday Soc.*, **23**, 400 (1927).

<sup>2</sup> Goldschmidt and Aarflot, *Z. physik. Chem.*, **122**, 371 (1926); cf. Unmack, Murray-Rust, and Hartley, *Proc. Roy. Soc.*, **127A**, 228 (1930).

<sup>3</sup> Wright, Murray-Rust, and Hartley, *J. Chem. Soc.*, **1931**, 199.

<sup>4</sup> Noyes and MacInnes, *J. Am. Chem. Soc.*, **42**, 239 (1920).

<sup>5</sup> *Chem. Soc. Ann. Repts.*, **1932**, 24.

<sup>6</sup> *J. Am. Chem. Soc.*, **46**, 555 (1924).

<sup>7</sup> *J. Am. Chem. Soc.*, **44**, 938 (1922).

<sup>8</sup> This equation follows from the square root dependence of the  $\ln \gamma$  on the concentration. Cf. Brönsted, *ibid.*, **42**, 765 (1920).

<sup>9</sup> Brönsted, *ibid.*, **44**, 638 (1922); Brönsted and LaMer, *ibid.*, **46**, 555 (1924).

$$-\ln \gamma = 3 \times 0.32z_1z_2\sqrt{\mu} \quad (8)$$

and

$$\theta = 0.32z_1z_2\sqrt{\mu} \quad (9)$$

where  $\mu$  is the ionic strength of the solution. Equation 8 is in agreement with Lewis and Randall's rule (see p. 309).

The validity of equations 5 and 6 is in itself an indication of the correctness of the theory of complete dissociation, inasmuch as it would be unlikely that such simple expressions would hold provided that the changes in the activity and osmotic coefficients with concentration were due, in part, to a displacement of electrolytic equilibrium.

A certain amount of indirect evidence has been brought forward from time to time which is not in harmony with the theory of complete dissociation;<sup>1</sup> and occasionally this concept has been the subject of acrimonious dispute. Notwithstanding this, however, there is fairly general acceptance at the present time of the idea that strong polar compounds are completely dissociated in dilute solutions, and that the conductance ratio,  $\Lambda_c/\Lambda_0$ , has not the significance attributed to it in the classical theory of Arrhenius.

**Milner's Theory.** The idea of complete dissociation was employed by Milner<sup>2</sup> to account for the behavior of strong electrolytes, the observed reduction in conductance with increasing concentration being attributed mainly to a decrease in the mobilities of the ions under the influence of the interionic forces. From a theoretical investigation of the influence of these forces, the conclusion was reached that changes in concentration will give rise to the same variations in the osmotic pressure and conductance of the "free" ions, by "free" ions being meant "those which momentarily have no mutual energy with any others." The effect of interionic forces is to produce an increase in the frequency of the occurrence of ions in an associated state, resulting in a decrease in the conductance and the osmotic pressure of the "free" ions, and in the molecular lowering of the freezing point. Milner<sup>3</sup> calculated what he called the "virial" of a mixture of ions, i.e., the sum of all the electrostatic forces in a chaos of equal numbers of oppositely charged particles, each force being multiplied by the distance over which it acts, and therefrom calculated values for the molecular lowering of the freezing point in aqueous solutions of a completely dissociated uniunivalent electrolyte.

<sup>1</sup> Cf. Schneider and Bradley, *ibid.*, **45**, 1121 (1923); Dawson, *Trans. Faraday Soc.*, **15**, 152 (1919); Arrhenius, *ibid.*, **15**, 15 (1919); Harkins, *Proc. Natl. Acad. Sci. U. S.*, **6**, 601 (1920); Kendall, *J. Am. Chem. Soc.*, **44**, 717 (1922); Dunn and Rideal, *J. Chem. Soc.*, **125**, 676 (1924).

<sup>2</sup> *Phil. Mag.*, **23**, 551 (1912).

<sup>3</sup> *Ibid.*, **25**, 742 (1912).



The excellent agreement between these values and those determined by Adams <sup>1</sup> for potassium chloride is shown in Table LXXXV.

TABLE LXXXV

MOLECULAR LOWERING OF THE FREEZING POINT OF UNIVALENT ELECTROLYTES

Concentration	Molecular Lowering of the Freezing Point	
	Milner	Adams
	MA	KCl
0.0001	3.709°	.....
0.001	3.687°	.....
0.002	3.674°	3.658°
0.005	3.649°	3.643°
0.01	3.621°	3.609°
0.02	3.582°	3.570°
0.05	3.506°	3.505°
0.1	3.418°	3.451°

Milner's theory is noteworthy for its simplicity and its few arbitrary assumptions, but it is obviously incomplete. It fails to account for the applicability of the law of mass action to solutions in solvents of low dielectric constants, where the interionic forces should be greater than in water; and up to the present Milner has failed to obtain an expression for the conductance of solutions as a function of the concentration.

**Debye and Hückel's Theory.** Like Milner, Debye and Hückel <sup>2</sup> assumed complete dissociation at *all* concentrations and attributed the deviations from the limiting laws, exhibited by solutions of strong electrolytes, to electrical forces between the ions and the ions and the molecules of the solvent. Even though this theory cannot be regarded as complete, its scope and nature indicate that a most decided advance has

<sup>1</sup> *J. Am. Chem. Soc.*, **37**, 481 (1915).

<sup>2</sup> *Physik. Z.*, **24**, 185, 305 (1923); Debye, *Rec. trav. chim.*, **42**, 597 (1923); *Physik. Z.*, **25**, 97 (1924); Hückel, *ibid.*, **26**, 93 (1925); *Ergeb. exakt. Naturw.*, **3**, 199 (1925); Debye and Pauling, *J. Am. Chem. Soc.*, **47**, 2129 (1925). For a critical presentation of this theory, the reader is referred to Noyes, *J. Am. Chem. Soc.*, **46**, 1080 (1924); cf. also LaMer, *Trans. Am. Electrochem. Soc.*, **51**, 507 (1927).

been made in our understanding of the problem of the behavior of dilute solutions of electrolytes, and even in its present form it has been found to be very useful. Moreover, the experimental verification which the theory has so far received may be regarded as strong support of the hypothesis of complete dissociation.

The starting point in the development of the theory is Milner's fundamental idea of an **ionic atmosphere**, resulting from a non-random distribution of the ions about a given ion. This ionic atmosphere arises from the existence of Coulomb forces which cause an excess of negative ions to be in the vicinity of a positive ion, and *vice versa*. These forces acting alone would bring about a lattice arrangement of the ions; but any regularity in the spatial distribution of the ions tends to be prevented by their thermal vibrations, the intensity of which increases as the temperature is raised. The properties of a solution of an electrolyte are, therefore, largely due to the interplay of these effects: Coulomb forces and thermal vibrations. As the concentration of the solution is decreased, the distance between the ions increases; and at very low concentrations the ions are separated to such an extent that their mutual attractions are insignificant and a *random* distribution prevails, i.e., the solution obeys the simple gas laws. By calculating the excess electrical work involved in the rearrangement of the relative positions of the ions, brought about by isothermal dilution, Debye and Hückel were able to calculate correctly the deviations from the simple gas laws in terms of the osmotic coefficient of the solvent, or in terms of the activity coefficient of the ions.

The calculation of this work, either directly<sup>1</sup> or by means of the electrical mutual *potential* resulting from an unequal distribution of the ions, requires a knowledge of the average electric potential of an ion due to the presence of a surrounding atmosphere of like and unlike ions. To determine this average electric potential, the following universally accepted generalizations are employed:

1. Coulomb's law of electrostatic force
2. Boltzmann's principle, which is used to calculate the distribution of the ions.

As previously mentioned, it is assumed as a working hypothesis that strong electrolytes are completely dissociated. Quoting from LaMer's paper:<sup>2</sup> "On this basis the following expression is obtained for the density of free electricity  $\rho$  in a unit of volume (1 cu cm) of solution in

<sup>1</sup> Debye, *Physik. Z.*, **25**, 97 (1924).

<sup>2</sup> *Trans. Am. Electrochem. Soc.*, **51**, 507 (1927). In this quotation a few changes have been made in Professor LaMer's nomenclature.

terms of  $\psi$  the *time average of the electric potential* and  $n$  the total number of ions present; namely, for a uniunivalent electrolyte,

$$\rho = n\epsilon \left( e^{-\frac{e\psi}{kT}} - e^{\frac{e\psi}{kT}} \right) \simeq -2n\epsilon \left( \frac{e\psi}{kT} \right) \quad (10)$$

where  $\epsilon$  is the unit charge on an ion equal to  $4.80 \cdot 10^{-10}$  esu;  $k$  represents Boltzmann's gas constant per molecule or  $R/N$ ; and  $T$  is the absolute temperature.

"This equation may be derived as follows: Consider a fixed positive ion, say a  $K^+$  ion in a KCl solution, and an element of volume  $dv$  in its neighborhood, as sketched in Fig. 83. If no interionic forces existed, the

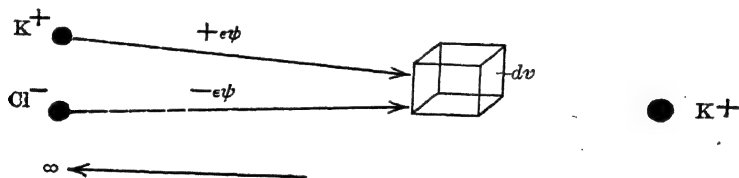


FIG. 83.

gas laws would apply to the solution, since an equal number of  $K^+$  ions and  $Cl^-$  ions as a consequence of their heat motion would enter and leave  $dv$  per unit of time, and a random distribution would prevail. Interionic forces, however, exist, and as a consequence the work  $+e\psi$  must be performed in order to bring a positive ion from infinity into  $dv$ . The ion thus acquires an additional potential energy  $+e\psi$ . A negative ion would acquire the potential energy  $-e\psi$ , thus losing potential energy.

"Now the Boltzmann principle states that the ionic distribution will be a function of the ratio of the electrical potential energy of each ion to its thermal energy  $kT$ , and is expressed as follows: On the average, there will be

$$n_+ = ne^{-\left(\frac{e\psi}{kT}\right)} dv \text{ positive ions}$$

and

$$n_- = ne^{+\left(\frac{e\psi}{kT}\right)} dv \text{ negative ions}$$

present in  $dv$ .

"The change in the amount of electricity in  $dv$  with time, due to the presence of an excess of positive or negative electricity at any given moment, is shown schematically in Fig. 84. Each hump represents the entrance and departure of a positive or negative ion in  $dv$ . The mean

density of electricity with respect to time is negative, since more  $\text{Cl}^-$  ions enter  $dv$  than do  $\text{K}^+$  ions, and quantitatively is equal to the sum of  $n_+$  and  $n_-$ , each ion being multiplied by its respective charge which in the present case is  $+\epsilon$  and  $-\epsilon$ , since the valence  $z$  equals  $\pm 1$ . This operation gives on eliminating  $dv$

$$\rho = \epsilon n_+ + (-\epsilon n_-) = n\epsilon \left( e^{\frac{-e\psi}{kT}} - e^{\frac{e\psi}{kT}} \right) = -2n\epsilon \sinh \left( \frac{e\psi}{kT} \right) \quad (11)$$

and since  $\frac{e\psi}{kT}$  is in general small we can replace the hyperbolic sine by its argument, obtaining equation 10.

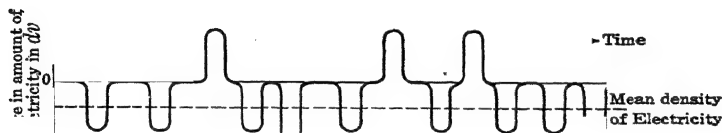


FIG. 84.

“The relation between the space variation of the electric potential  $\psi$  and the density of electricity  $\rho$  is given by the Poisson equation of electrostatics:

$$\nabla^2 \psi = \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d\psi}{dr} \right) = - \frac{4\pi\rho}{\epsilon} \quad (12)$$

where  $r$  represents distance,  $\pi = 3.1416$ ,  $\epsilon$  is the dielectric constant of the medium [and  $\nabla$  is the operator ‘nabla’ used in vector analysis]. By substituting for  $\rho$  its value in equation 10 and integrating we can eliminate  $r$  and determine  $\psi$  solely in terms of the valences and numbers of the respective ions, and the dielectric constant of the medium. The physical assumption involved in this step amounts to considering the  $\text{K}^+$  ion as though it were a sphere at the center of a larger hollow conducting sphere of radius  $r$  with the excess negative charge of the atmosphere of ions uniformly distributed upon the latter.

“If we designate

$$\kappa^2 = \frac{8\pi n\epsilon^2}{\epsilon kT} \quad (13)$$

equation 12 may be written

$$\nabla^2 \psi = \kappa^2 \psi \quad (14)$$

When 14 is integrated under the appropriate boundary conditions, namely, that  $\psi \rightarrow 0$  as  $r \rightarrow \infty$  and that the field strength  $\frac{-d\psi}{dr} \rightarrow \frac{\epsilon^2}{\epsilon a^2}$  when  $r = a$ , where  $a$  is considered for the moment as the radius of the ion,  $\bar{\psi}_i$  the total potential at the surface of the ion becomes

$$\bar{\psi}_i = \frac{\epsilon}{\epsilon a_i} - \frac{\epsilon \kappa}{\epsilon} \cdot \frac{1}{1 + \kappa a} \quad (15)$$

"The first member in 15 represents the potential of an ion in an ion-free medium of dielectric constant  $\epsilon$ , where it is not influenced by surrounding ions; the second member consequently represents the potential  $\psi_i$  at the surface of the ion, due to the presence of the surrounding atmosphere of ions, which is the quantity desired. When the concentration is small,  $\kappa$  is small, and the second member of 15 reduces to

$$\psi_i = \frac{-\epsilon}{\epsilon} \kappa \quad (16)$$

" $\kappa$  is a most important quantity in the theory, and from 16 we see that  $1/\kappa$  has the dimensions of distance. By the use of  $\kappa$  Debye and Hückel avoid the introduction of an average distance between ions based upon the cube root of the concentration, a procedure employed by many previous investigators, notably Ghosh, in their attempts to solve this problem. Debye and Hückel further show that the use of such an average distance is incorrect since the ions are not restricted to oscillating about fixed points as in a crystal, but are free to move about.  $1/\kappa$  is therefore called a 'characteristic or probability distance.'

"For aqueous solutions equation 13 yields for a uniunivalent salt

$$\kappa = 0.327 \sqrt{c} \cdot 10^{-8} \text{ cm}^{-1} \quad (17)$$

or, as shown later when ions of higher valence are present, the molar concentration  $c$  must be replaced by the ionic strength,  $\mu$ . In general

$$\kappa = 0.327 \sqrt{\mu} 10^{-8} \text{ cm}^{-1} \quad (18)$$

$1/\kappa$  is about ten times the diameter of an ion at  $0.01 \mu$ , but of the same order of magnitude for a  $1.0 \mu$  solution.

"Fortunately, the methods of Debye and Hückel can be extended to mixtures of ions of various concentrations and valences. In the general

case where we have an electrolyte yielding the following numbers of ions per molecule:

$$\nu_1, \dots \nu_i, \dots \nu_s, (\text{total} = \nu)$$

and the numbers (concentration) per cubic centimeter,

$$n_1, \dots n_i, \dots n_s$$

corresponding to ions of the sorts 1,  $\dots$   $i$ ,  $\dots$   $s$  and possessing the valences

$$z_1, \dots z_i, \dots z_s$$

where  $z$  is a whole number, either positive or negative, and these ions are in turn dissolved in a solvent containing various other ions having the numbers per cubic centimeter,

$$n_1, \dots n_i, \dots n_s,$$

and corresponding valences, it becomes necessary to consider the charge of each ion  $e_i$  as equal to  $z_i e$ , and employ summation methods. In the general case

$$\kappa = \sqrt{\frac{4\pi\epsilon^2}{\epsilon k T}} \sqrt{\sum n_i z_i^2} \quad (19)$$

and

$$\psi_i = \frac{-z_i \epsilon \kappa}{\epsilon} \cdot \frac{1}{1 + \kappa a_i} \simeq \frac{-z_i \epsilon \kappa}{\epsilon} \quad (20)$$

where the term  $\sum n_i z_i^2$  is nothing other than twice the ionic strength when expressed as number of ions per cubic centimeter. When the concentration is stated in terms of moles per liter, 19 reduces to the simple form 18."

With the value given in equation 20 for the potential at the surface of an ion due to the ionic atmosphere, an expression for the osmotic coefficient of the solvent may be derived by thermodynamic methods. For dilute solutions this derivation gives

$$f_0 = 1 - w \frac{\epsilon^2}{6\epsilon k T} \sqrt{\frac{4\pi\epsilon^2}{\epsilon k T}} \cdot n \sum \nu_i \quad (21)$$

where  $\nu_i$  is the number of ions of the  $i^{\text{th}}$  sort formed by the dissociation of one molecule of electrolyte,  $n = Nc/1000$ , and  $w$ , a *valence factor*, is given by

$$w = \left[ \frac{\sum \nu_i z_i^2}{\sum \nu_i} \right]^{3/2} \quad (22)$$

Corresponding to the number and valence of the ions,  $w$  has for uniunivalent, biunivalent, bibivalent, triunivalent and tribivalent electrolytes the value: 1,  $2\sqrt{2} = 2.83$ ,  $4\sqrt{4} = 8$ ,  $3\sqrt{3} = 5.2$ , and  $6\sqrt{6} = 16.9$ , respectively.

By combining equations 3 and 21, we obtain for the osmotic deviation of the solvent the expression

$$\Theta = 1 - f_0 = w \frac{\epsilon^2}{6\epsilon kT} \sqrt{\frac{4\pi\epsilon^2}{\epsilon kT} \cdot n \Sigma \nu_i} \quad (23)$$

This equation shows that for dilute solutions the osmotic deviation is proportional to both the square root of the molal concentration,  $c$ , and a valence factor, and is inversely proportional to the  $\frac{3}{2}$  power of the dielectric constant of the solvent. On substituting the following values,  $\pi = 3.14159$ ,  $T = 273$  (for dilute aqueous solutions),  $\epsilon = 4.771 \times 10^{-10}$  esu,  $n$  (the number of molecules per cubic centimeter)  $= 6.06 \times 10^{20} c$  (where  $c$  is the molal concentration),  $k = 1.346 \times 10^{-16}$  erg, and  $\epsilon = 88.23$  (at  $0^\circ \text{C}$ ), equation 23 reduces to

$$\Theta = 0.270w\sqrt{\nu c} \quad (24)$$

where  $\nu$  is the number of ions produced by one molecule of the electrolyte. Since, for an electrolyte yielding *two kinds of ions*,

$$c\nu = \frac{c_1 z_1^2 + c_2 z_2^2}{z_1 z_2} = \frac{2\mu}{z_1 z_2} \quad (25)$$

for salts of this type equation 24 may be expressed in terms of the ionic strength, as follows:

$$\Theta = 0.38z_1 z_2 \sqrt{\mu} = \beta z_1 z_2 \sqrt{\mu} \quad (26)$$

The Debye and Hückel constant,  $\beta = 0.38$ , is a universal constant, depending only upon the absolute temperature ( $T$ ), the unit charge of electricity ( $\epsilon$ ), Boltzmann's constant ( $k$ ), and the dielectric constant of the solvent ( $\epsilon$ ). Equation 25 is essentially the same as equation 9.

Debye<sup>1</sup> showed that, at very low concentrations, the osmotic equation of state assumes the form

$$PV = kT[\nu c - \ln(1 - \Theta)] \quad (27)$$

<sup>1</sup> *Physik. Z.*, **25**, 97 (1924).

By combining equation 6 with equations 23, 24, and 26, respectively, we obtain the following relations <sup>1</sup> for the activity coefficient of a *salt*:

$$\ln \gamma = -w \frac{\epsilon^2}{2\epsilon kT} \sqrt{\frac{4\pi\epsilon^2}{\epsilon kT} \cdot n\Sigma\nu_i} \quad (28)$$

$$\ln \gamma = -0.81w\sqrt{\nu c} \quad (29)$$

and, for an electrolyte yielding two kinds of ions,

$$\ln \gamma = -1.14z_1z_2\sqrt{\mu} \quad (30)$$

or

$$\log \gamma = -0.505z_1z_2\sqrt{\mu} \quad (31)$$

The activity coefficient of an *ion* is

$$\ln \gamma_i = -1.14z_i^2\sqrt{\mu} \quad (32)$$

From a chemical standpoint, these equations are probably the most important expressions of the Debye and Hückel theory. Equation 32 shows that the activity coefficients of all ions of the same valence are identical in solutions of the same ionic strength, a conclusion which is in agreement with Lewis and Randall's rule (p. 309).

TABLE LXXXVI  
VALUES OF THE FUNCTION  $\sigma$

$a\kappa$	$\sigma$	$a\kappa$	$\sigma$	$a\kappa$	$\sigma$	$a\kappa$	$\sigma$
0.00	1.000	0.40	0.598	0.90	0.370	3.00	0.1109
0.05	0.929	0.50	0.536	1.00	0.341	3.50	0.0898
0.10	0.855	0.60	0.486	1.50	0.238	4.00	0.0742
0.20	0.759	0.70	0.441	2.00	0.176	4.50	0.0628
0.30	0.670	0.80	0.403	2.50	0.136	5.00	0.0540

<sup>1</sup> It must be remembered that these equations are valid only for very dilute solutions. The negative value of  $\ln \gamma$  in equations 6 and 28 to 32 cannot account for the activity coefficient having a value greater than unity (see Table LXXXIV in the preceding chapter). Since the effect of the interionic forces is to cause a deformation of the electron orbits of the ions with the development of polarity, the close approach of two ions in water establishes a repulsive force between them which may overcome the ordinary attraction and so *increase* the activity coefficient. Accordingly, for concentrated solutions Hückel has shown, *Physik. Z.*, **26**, 93 (1925), that a second term must be added to the right-hand member of these equations.



When the concentration of solutions of strong electrolytes is higher than  $0.01 \mu$ , the factor  $1/(1 + \kappa a_i)$ , equation 20, must be considered. For such solutions the expression for the osmotic deviation becomes

$$\Theta = 0.270w\sqrt{\nu c} \cdot \sigma \quad (33)$$

where  $\sigma$  is a function involving  $\kappa$  and  $a$ , the **effective ionic diameter**, or the distance of closest approach of two ions. The value of  $a$  is the average of all the  $a_i$  values. In Table LXXXVI are given values of the function  $\sigma$  corresponding to values of  $\kappa a$  from 0.0 to 5.0.<sup>1</sup>

**Experimental Verification of Debye and Hückel's Theory.** Debye and Hückel used all available freezing-point data to verify equation 33. Though their results cannot be said to establish their theory, owing to the meagerness of the data for very dilute solutions, the agreement be-

TABLE LXXXVII  
THE OSMOTIC DEVIATION OF ELECTROLYTES

$\nu c$	$\sqrt{\nu c}$	$\Theta_{\text{Observed}}$	$\Theta_{\text{Calculated}}$
KCl ( $a = 3.76 \times 10^{-8}$ cm)			
0.0100	0.100	0.0214	0.0237
0.0193	0.139	0.0295	0.0313
0.0331	0.182	0.0375	0.0392
0.0633	0.252	0.0485	0.0499
0.116	0.341	0.0613	0.0618
MgSO <sub>4</sub> ( $a = 3.35 \times 10^{-8}$ cm)			
0.0107	0.103	0.199	0.179
0.0262	0.162	0.258	0.248
0.0534	0.231	0.306	0.311
0.0976	0.312	0.349	0.368
0.138	0.372	0.392	0.400
K <sub>2</sub> SO <sub>4</sub> ( $a = 2.69 \times 10^{-8}$ cm)			
0.0121	0.110	0.0729	0.0724
0.0312	0.176	0.101	0.108
0.0527	0.229	0.128	0.132
0.0782	0.280	0.147	0.152
0.267	0.516	0.220	0.217

<sup>1</sup> Debye and Hückel, *Physik. Z.*, **24**, 185 (1923).

tween the observed and calculated values of the osmotic coefficient is good. This is illustrated by the data in Table LXXXVII.<sup>1</sup> The results of Hovorka and Rodebush's measurements<sup>2</sup> of the freezing points of seven electrolytes having concentrations between 0.01 and 0.001 molal show a "rather remarkable agreement with the values deduced from the Debye and Hückel equation." Further confirmations of the theory have been obtained in non-aqueous solvents, such as alcohol,<sup>3</sup> and glacial acetic acid and liquid ammonia.<sup>4</sup> Moreover, the correctness of the simple Debye and Hückel equation as a limiting law at infinite dilution has been confirmed by several lines of critical examination.<sup>5</sup>

Important confirmation<sup>6</sup> of the validity of the theory has been obtained as the result of very accurate measurements of the solubility of very slightly soluble salts of the cobaltammine family in solutions of electrolytes of various valence types. The relation between the activity coefficient and the solubility is obtained as follows. In a saturated solution the activity of the solute is equal to that of the solid salt, and this remains unchanged in the presence of the added salt, even though the solubility is altered. If  $S$  and  $S'$  are the solubilities in pure water and in a salt solution, and  $\gamma$  and  $\gamma'$  the activity coefficients in the same media, then

$$= \frac{a_2^{1/2}}{S} \quad \text{and} \quad \frac{a_2^{1/2}}{S'}$$

Hence

$$-\log \gamma' = \log \frac{S'}{S} - \log \gamma \quad (34)$$

Since the salt is very slightly soluble, its activity coefficient in pure water is equal to unity, and

$$-\log \gamma' = \log \frac{S'}{S} = 0.505 z_1 z_2 \sqrt{\mu} \quad (35)$$

The experimental results obtained verify in a striking manner (1) the principle of ionic strength, (2) the correctness of the valence factor,  $w$ , and (3) the correctness of the value of the Debye-Hückel constant (equation 26).

<sup>1</sup> Debye and Hückel, *Physik. Z.*, **24**, 202 (1923).

<sup>2</sup> *J. Am. Chem. Soc.*, **47**, 1614 (1925).

<sup>3</sup> Noyes and Baxter, *ibid.*, **47**, 2122 (1925).

<sup>4</sup> Webb, *ibid.*, **48**, 2263 (1926).

<sup>5</sup> Cf. Scatchard, *Physik. Z.*, **33**, 145 (1932); Scatchard and Kirkwood, *ibid.*, **33**, 297 (1932).

<sup>6</sup> Brönsted and LaMer, *J. Am. Chem. Soc.*; **46**, 555 (1924); LaMer, King, and Mason, *ibid.*, **49**, 363 (1927); cf. also Davies and Blagden, *J. Chem. Soc.*, **1930**, 949; Davies, *ibid.*, **1930**, 2410, 2421.

Some evidence has been brought forward which is in apparent conflict with the theory. Anomalous effects which had been noted for solubility measurements at moderate concentrations, involving saturating salts with high-valence cations in the presence of solvent salts with high-valence anions, have been found to persist out to very high dilutions ( $0.0005 \mu$ ).<sup>1</sup> The data obtained for the freezing points of solutions of hydrogen chloride, lead nitrate, and thallous chloride are not in agreement with the theory<sup>2</sup> and the determination, by electromotive-force measurements, of the activity coefficients of hydrochloric acid at extreme dilutions leads to a considerably lower value of the Debye and Hückel constant than that given in equation 26.<sup>3</sup> However, certain anomalies of the theory have been explained by Bjerrum<sup>4</sup> on the assumption that the effective dielectric constant of the solvent decreases in the vicinity of the ions.

In their development of the simple theory, Debye and Hückel, besides making certain approximations, assumed that all forces other than the Coulomb forces could be neglected, that no correction was necessary for the overlapping of ionic atmospheres, and that the solvent between the ions had the same properties as the pure solvent in bulk. Accordingly, although equation 20 is valid for very dilute solutions of electrolytes, it may be expected to fail at higher concentrations. This failure has been found to occur at about 0.01 normal for aqueous solutions of uniunivalent salts at  $25^\circ$ ,<sup>5</sup> and at lower concentrations when, owing to a smaller dielectric constant or to higher valences of the ions, the interionic forces are increased. With small ions or with ions of high valence, the simple theory leads to ionic diameters which are either unreasonably small or negative.<sup>6</sup>

In view of these limitations, attempts have been made to extend the range of the validity of the ionic atmosphere calculations, notably by Debye and Hückel<sup>7</sup> and by Gronwall, LaMer, and Sandved,<sup>8</sup> to more concentrated solutions. These extensions lead to complicated equations by means of which, so far as activity coefficients are concerned, it has been found possible to give an adequate representation of facts up to

<sup>1</sup> LaMer and Mason, *J. Am. Chem. Soc.*, **49**, 410 (1927).

<sup>2</sup> Randall and Vanselow, *ibid.*, **46**, 2418 (1924).

<sup>3</sup> Nonhebel, *Phil. Mag.*, [vii] **2**, 1085 (1926).

<sup>4</sup> *Trans. Faraday Soc.*, **23**, 445 (1927).

<sup>5</sup> Cf. Kramer, *Proc. Konink. Akad. Wetenschappen Amsterdam*, **30**, 145 (1927); Fowler, *Trans. Faraday Soc.*, **23**, 434 (1927).

<sup>6</sup> Cf. Müller, *Physik. Z.*, **28**, 324 (1927); **29**, 78 (1928); Gronwall, *Proc. Natl. Acad. Sci. U. S.*, **13**, 198 (1927).

<sup>7</sup> *Physik. Z.*, **24**, 185 (1923).

<sup>8</sup> *Ibid.*, **29**, 358 (1928).

concentrations of about 0.1 normal. Solubility data in both aqueous and non-aqueous solution have been successfully interpreted by the extension of the theory made by Gronwall, LaMer, and Sandved.<sup>1</sup>

**The Debye-Hückel Theory and Electrolytic Conductance.** The change in the equivalent conductance of strong electrolytes with concentration was treated by Debye and Hückel<sup>2</sup> on the same basis as the osmotic (thermodynamic) properties of their solutions. Under the influence of an applied electric field the ions move towards the electrodes. This movement gives rise to two retarding effects, resulting in a decrease in the mobility of the ions. The first of these, a *dissymmetry* effect, is due to the opposing electric force resulting from a disturbance of the surrounding ionic atmosphere. Since time is required for the atmosphere to adjust itself to this disturbance, an unsymmetrical force will be exerted on the ion. This tends to reduce its mobility. The mobility of the ions is further decreased by an *electrophoretic* effect due to the counter current of the solvent produced by the ions comprising the ionic atmosphere.

From a consideration of these effects, Debye and Hückel deduced the following expression for the conductance of a  $z$ -valent electrolyte:

$$\frac{\Lambda_0 - \Lambda_c}{\Lambda_0} = \left[ \frac{K_1}{(\epsilon T)^{3/2}} w_1 + w_2 b \sqrt{2c} \right] \quad (36)$$

where  $K_1$  and  $K_2$  are universal constants,  $b$  is the average radius of the ions,  $w_1$  and  $w_2$  are valence factors, and the other quantities have their previous significance. The first and second terms of the right-hand member of equation 36 are dissymmetry and electrophoretic terms, respectively. For dilute aqueous solutions equation 36 reduces to

$$\Lambda_c = \Lambda_0 - x\sqrt{c} \quad (37)$$

an expression which is identical with the empirical relation found by Kohlrausch (equation 7a, Chapter V).

**The Onsager Equation.** Onsager pointed out<sup>3</sup> that in their calculation of the dissymmetry effect Debye and Hückel failed to take into account the influence of the Brownian movement of the ions, and also that their calculation is valid only when the cations and anions have equal mobili-

<sup>1</sup> Cf. Seward and Schumb, *J. Am. Chem. Soc.*, **52**, 3962 (1930); LaMer, Gronwall, and Greiff, *J. Phys. Chem.*, **35**, 2245 (1931); Seward and Hamblet, *J. Am. Chem. Soc.*, **54**, 554 (1932); Neuman, *ibid.*, **54**, 2195 (1932); School, Hutchison, and Chandlee, *ibid.*, **55**, 3081 (1933).

<sup>2</sup> *Physik. Z.*, **24**, 305 (1923).

<sup>3</sup> *Ibid.*, **27**, 288 (1926); **28**, 277 (1927).

ties. Taking these factors into consideration, he modified their calculations and deduced an equation having the same general form as that of Debye and Hückel. For a  $z$ -valent electrolyte Onsager's equation takes the form

$$\Lambda_0 - \Lambda_c = \left[ \frac{0.986 \times 10^6}{(\epsilon T)^{3/2}} (2\sqrt{2} - 2) \Lambda_0 z^{3/2} + \frac{58.0}{(\epsilon T)^{3/2} \eta} \cdot z^{3/2} \right] \sqrt{c} \quad (38)$$

where  $\eta$  is the viscosity of the solvent. For uniunivalent electrolytes at 25° this equation reduces to:

$$\Lambda_c = \Lambda_0 - (0.288 \Lambda_0 + 59.8) \sqrt{c} \quad \text{for water} \quad (39)$$

$$\Lambda_c = \Lambda_0 - (0.957 \Lambda_0 + 158.1) \sqrt{c} \quad \text{for methyl alcohol} \quad (40)$$

$$\Lambda_c = \Lambda_0 - (1.256 \Lambda_0 + 87.8) \sqrt{c} \quad \text{for ethyl alcohol} \quad (41)$$

Equation 38 may also be written in the form

$$\Lambda_c = \Lambda_0 - (r \Lambda_0 + s) \sqrt{c} \quad (42)$$

where  $r$  and  $s$  are constants and  $(r \Lambda_0 + s) = A$  is the limiting theoretical slope. On solving this equation for  $\Lambda_0$  we obtain

$$\Lambda_0 = \frac{\Lambda_c + s \sqrt{c}}{1 - r \sqrt{c}} \quad (43)$$

For aqueous solutions at 25°,  $r = 0.2274$  and  $s = 59.79$ ; at 18° these values are 0.225 and 50.3, respectively.

A large number of conductance measurements, both in aqueous and non-aqueous solution, has been carried out for the purpose of testing Onsager's equation.<sup>1</sup> It has been found that the curve obtained by plotting  $\Lambda_c$  against  $\sqrt{c}$  is linear in dilute solutions, but the slope is not always in agreement with the calculated value.

*The Shedlovsky Equation.* Although Onsager's equation is in close agreement with experimental data at low concentrations, holding for solutions of uniunivalent strong electrolytes up to a concentration of 0.002 normal, it is strictly valid only as a limiting expression. By the addition of a single term to equation 43, Shedlovsky,<sup>2</sup> has extended its range up to concentrations of the order of 0.1 normal for aqueous solu-

<sup>1</sup> Cf., for example, Martin, *J. Chem. Soc.*, 1928, 3270; 1930, 530; Saxton and Langer, *J. Am. Chem. Soc.*, 55, 3638 (1933); MacInnes, Shedlovsky, and Longworth, *Chem. Revs.*, 13, 29 (1933); Jones and Bickford, *J. Am. Chem. Soc.*, 56, 602 (1934); Dippy, Jenkins, and Page, *J. Chem. Soc.*, 1939, 1386.

<sup>2</sup> *J. Am. Chem. Soc.*, 54, 1405 (1932).

tions of strong electrolytes. This new relation between equivalent conductance and concentration has the form

$$\Lambda_0 = \frac{\Lambda_c + s\sqrt{c}}{1 - r\sqrt{c}} - Bc \quad (44)$$

or

$$\Lambda_c = \Lambda_0 - A\sqrt{c} + Bc(1 - r\sqrt{c}) \quad (45)$$

where  $B$  is an empirical constant. It is evident that this equation reduces to the Onsager equation at low concentrations.

Equation 45 has been used to calculate the conductances of a number of uniunivalent electrolytes at 18°.¹ Some of the results of these calculations are given in Table LXXXVIII. Although, as is shown by the data

TABLE LXXXVIII  
EQUIVALENT CONDUCTANCES AT 18°

$c$	LiNO <sub>3</sub>		NaCl		KF		KSCN		KI	
	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.
0	95.1		108.5		111.2		120.6		130.3	
0.001	92.9	92.9	106.2	106.3	108.9	108.9	118.3	118.4	127.9	128.0
0.005	90.4	90.3	103.6	103.5	106.2	106.2	115.5	115.5	125.1	125.1
0.01	88.6	88.6	101.7	101.7	104.4	104.3	113.7	113.7	123.3	123.2
0.02	86.5	86.4	99.4	99.4	102.0	101.9	111.4	111.3	120.8	120.8
0.05	82.6	82.7	95.4	95.5	97.7	97.7	107.6	107.5	116.9	117.0
0.07	81.1	81.1	....	....	95.9	96.0	106.0	106.1	115.4	115.5
0.10	79.4	79.2	92.0	91.8	94.0	94.0	104.5	104.5	113.8	113.8
$A$	71.7		74.7		75.5		77.4		79.6	
$B$	75		76		71		90		93	

in Table LXXXVIII, equation 45 gives results for aqueous solutions of uniunivalent electrolytes which are in excellent agreement with experiment up to concentrations of 0.1 normal, it does not hold so well for solutions of the alkaline-earth chlorides.²

It has been pointed out³ that, in any general quantitative description of electrolytic behavior, there should be taken into consideration the specific interaction between solute and solvent (which can occur even in

¹ Shedlovsky, *ibid.*, **54**, 1405 (1932); cf. also Shedlovsky, Brown, and MacInnes, *Trans. Electrochem. Soc.*, **66**, 237 (1934).

² Shedlovsky and Brown, *J. Am. Chem. Soc.*, **56**, 1066 (1934).

³ McIntosh, Mead, and Fuoss, *ibid.*, **62**, 506 (1940).

solutions of strong electrolytes) and those forces other than Coulomb interaction between the ions.

**The Wien Effect.** In 1927 Max Wien discovered that the conductance of a solution of an electrolyte increased with the potential gradient when very high gradients (e.g., 300,000 volts per centimeter) were employed; in other words, under such high field strengths Ohm's law was no longer valid.<sup>1</sup> Wien showed that this effect was a general property of electrolytic solutions, and that it depended on the concentration and valence of the ions and on the specific nature of the solute and solvent. He showed further that for extremely high electric fields the conductance tended towards a constant limiting value, which corresponded nearly to that of  $\Lambda_0$  as ordinarily measured in low fields. With decreasing concentration of electrolyte, this limiting value was approached at lower field strengths.

Wien's striking discovery, which has played an important role in the development of the theory of electrolytic solutions, may be interpreted in terms of the time of relaxation of the ionic atmosphere.<sup>2</sup> In a potential gradient of 500,000 volts per centimeter, the ions in a 0.001 *N* aqueous solution of potassium chloride at 25° would move, during the time of relaxation, through a distance 35 times greater than the radius of their atmospheres. Consequently, the ions would become separated from their atmospheres, their retarding effects would disappear, and the conductance would rise to that at zero concentration.

**The Degree of Dissociation of Strong Electrolytes.** Midway between the theory of complete dissociation and that which assumes the existence of undissociated molecules is Bjerrum's theory of "ion association."<sup>3</sup> According to this theory, when two oppositely charged ions approach each other closer than a certain minimum distance they form an ion pair, this being equivalent to an undissociated molecule without involving a covalent linkage. The minimum distance is given by the expression

$$r_{\min.} = \frac{e^2 z^2}{2\epsilon kT} \quad (46)$$

For aqueous solutions of uniunivalent electrolytes  $r_{\min.}$  has the value 3.52 Å at 18°. By applying the law of mass action to the equilibrium between free ions and ion pairs, Bjerrum has calculated a series of degrees of "ion association" which increase with concentration and also with decrease in the radii of the ions considered. Fajans has cited

<sup>1</sup> *Physik. Z.*, **28**, 834 (1927); **29**, 751 (1928); **32**, 545 (1931). For reviews of the Wien effect, see Ekstrom and Schmelzer, *Chem. Revs.*, **24**, 367 (1939); Deubner, *Physik. regeln. Ber.*, **8**, 97 (1940).

<sup>2</sup> Joos and Blumentritt, *Physik. Z.*, **28**, 836 (1927).

<sup>3</sup> *Ergeb. exakt. Naturw.*, **5**, 125 (1926).

evidence<sup>1</sup> in support of the conclusion that solutions of strong electrolytes contain appreciable amounts of undissociated particles.

Since Bjerrum's hypothesis postulates the existence in solution of something equivalent to undissociated molecules, it becomes desirable to be able to determine the "true" degree of dissociation of electrolytes. The derivation of this quantity from conductance measurements has been treated by Onsager,<sup>2</sup> Davies,<sup>3</sup> and others. In this treatment it has been assumed that the decrease in equivalent conductance with increasing concentration is due jointly to (1) a decrease in the mobility of the ions caused by interionic forces and (2) an increase in the number of undissociated molecules. Since the first of these effects can be calculated from the Debye-Hückel equation, the magnitude of the second can be ascertained. Davies' method of making the calculation is as follows.

If  $\alpha$  is the true degree of dissociation of an electrolyte at a concentration where the equivalent conductance is  $\Lambda_c$ , and  $\Lambda_0$  is its limiting value, then  $\alpha = \Lambda_c/\Lambda_x$ , where  $\Lambda_x$  is the equivalent conductance of the *completely dissociated solute at the same ion concentration*. Since the concentration of each of the ions is  $c_i = c\Lambda_c/\Lambda_x$ , it follows from equation 39 that for an aqueous solution of a uniunivalent electrolyte at 25°

$$\Lambda_x = \Lambda_0 - (0.228\Lambda_0 + 59.8)\sqrt{c\Lambda_c/\Lambda_x} \quad (47)$$

This cubic equation in  $\Lambda_x$  may be solved as such, or  $\Lambda_x$  may be evaluated by successive approximations, and from the values obtained the true degree of dissociation,  $\Lambda_c/\Lambda_x$ , may be calculated. From the degree of dissociation the true concentration of the ions,  $c_i$ , and that of the undissociated molecules,  $c_u$ , may be obtained.

As we have already seen (equation 10, Chapter XIV), the activity coefficient of an ion and that of the undissociated molecules are given by the expressions

$$\gamma_i = \frac{a_i}{c_i} \quad \text{and} \quad \gamma_u = \frac{a_u}{c_u}$$

Combining these with equation 6, Chapter XIV, we obtain for the mass-action constant

$$K = \frac{c_i^2 \cdot \gamma_i^2}{c_u \cdot \gamma_u} \quad (48)$$

or for dilute solutions, when  $\gamma_u$  may be put equal to unity,

$$K = \frac{c_i^2 \cdot \gamma_i^2}{c_u} \quad (49)$$

<sup>1</sup> *J. Chem. Phys.*, **9**, 283 (1941).

<sup>2</sup> *Trans. Faraday Soc.*, **23**, 351 (1927).

<sup>3</sup> *Physik. Z.*, **28**, 277 (1927).



Since at very low concentrations it is evident from equation 32 that  $-\log \gamma_i = A\sqrt{c_i}$ , where  $A$  is a constant, equation 49 may be written

$$\log \frac{c_i^2}{c_u} = \log K + 2A\sqrt{c_i} \quad (50)$$

The constancy of this relation may be tested graphically by plotting the left-hand member against  $\sqrt{c_i}$ , when there should be obtained a straight line of slope  $2A$ , whose intercept at  $c = 0$  is  $\log K$ . Once  $K$  has been calculated from conductance data at very low concentrations, the degree of dissociation at higher concentrations can be found from activity measurements. Unfortunately, the method does not lend itself to the study of solutions in which dissociation is very nearly complete, since it is susceptible to considerable error unless the proportion of undissociated electrolyte is appreciable.

The method just described has been employed by Davies and his associates<sup>1</sup> to determine the degrees of dissociation and the mass-action constants of a number of salts and acids. The values obtained for the sulphates of zinc and several other bivalent metals indicate extensive ion association in solutions of these electrolytes. Since, however, there exists real evidence that zinc sulphate, at least, is completely dissociated, the accuracy of the method must be regarded with considerable doubt when applied to solutions of bibivalent salts.<sup>2</sup> Nevertheless, although subject to certain limitations, "the Davies method of treating conductivity data is probably the least equivocal way of gaining information as to the degree of dissociation of electrolytes."<sup>3</sup>

**Summary.** In the early years of the theory of electrolytic dissociation various explanations were put forward to account for the anomalous behavior of strong electrolytes; and the effects of viscosity, hydrate formation, and complex-ion formation studied without throwing much light on the problem. These difficulties led to the rejection of the fundamental assumptions of Arrhenius, and to the substitution of an hypothesis of complete dissociation of strong electrolytes at *all* concentrations, variations in the properties of the solutions with concentration being attributed to changes in the electric forces between the ions and *not to a change in the number of the ions*. Several new theories of electrolytic solutions, based upon this concept, were put forward. Of these, the theory of Debye and Hückel appears to approach a complete solution of the problem of strong electrolytes in dilute solution.

<sup>1</sup> *Trans. Faraday Soc.*, **23**, 351 (1927); **26**, 592 (1930); **27**, 621 (1931); **28**, 609 (1932).

<sup>2</sup> Cowperthwaite, *ibid.*, **29**, 593 (1933).

<sup>3</sup> Wolfenden, *Chem. Soc. Ann. Repts.*, **1932**, 29.

The Debye and Hückel theory, which attributes the properties of strong electrolytes to an interplay of the electrical forces between the ions and the thermal vibrations of the ions, leads to equations which can be tested experimentally. The accuracy with which experimental data fit these equations and their extensions shows that the theory is successful in accounting for the thermodynamic (osmotic) properties of dilute solutions of strong electrolytes. With the more complicated phenomena of electrolytic conductance the success of the theory is more limited, probably because other factors not yet brought to light must be considered. Although the Debye and Hückel theory cannot yet be regarded as complete, its scope and nature indicate that a decided advance has been made in our understanding of dilute solutions of strong electrolytes, and, even in its present form, it has proved most useful. The interionic attraction theory can also be applied to weak electrolytes.

While the successful application of the Debye-Hückel equations indicates that strong electrolytes are completely dissociated in dilute solution, there is evidence that even moderately concentrated solutions of these electrolytes may contain a small fraction of "undissociated" molecules. By this term is meant any modification in the distribution of the ions, and it includes associated ions, ion complexes, ion pairs, and covalent molecules.

In a review of our knowledge of electrolytes in non-aqueous solution, Kraus<sup>1</sup> points out that much remains to be done in this field and summarizes a number of lines of future investigation as follows:

"A greater number of solvent and solute types needs to be investigated, including solvents having dielectric constants higher than that of water, as well as lower. The influence of temperature requires investigation over the widest possible range. Electrolytes, other than those commonly employed, need to be studied over a wide range of conditions, particularly such electrolytes as yield solutions of low conducting power. The study of solvents should be extended to include solvents of high viscosity, including plastic media. Two-phase systems and surface phenomena require attention. Our knowledge of colloidal electrolytes in non-aqueous solution is very deficient. The interaction of ions with solvent molecules and the precise nature of the ions themselves remain to be determined. Mixtures of electrolytes require investigation.

"On the theoretical side, the outstanding problem is that of concentrated solutions. Many experimental data are available, but they remain uncorrelated. There is, as yet, no theory of concentrated solutions of electrolytes. In solvents of low dielectric constant, there is reason to believe that in physically dilute systems ( $C = 10^{-2}$  to  $10^{-5}$  N)

<sup>1</sup> *J. Franklin Inst.*, **225**, 706 (1938).

a multiplicity of equilibria exists between neutral and charged molecule, of many different degrees of complexity. In more concentrated systems phenomena may intervene of an entirely different type. In the light of our present knowledge, it seems safe to predict that the solution of the problem of electrolytes will probably not be found through a mere extension of the limiting laws that hold only at very low concentrations."

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### PROBLEMS

1. Using the necessary data given in Tables LXXXVI and LXXXVII, check the values in the latter table for the osmotic deviation of the solutions of potassium chloride, magnesium sulphate, and potassium sulphate.
2. Calculate the ionic strength of each of the solutions given in Table LXXXVII.

## CHAPTER XVI

### RELATIONS BETWEEN CHEMICAL STRUCTURE AND THE DISSOCIATION CONSTANT

The majority of the physical properties of chemical compounds are both additive and constitutive. Only one purely additive property is known, namely, weight or mass, the mass of a chemical compound being exactly equal to the sum of the masses of its constituents. With the exception of mass, all properties are affected more or less by constitution. The most strongly constitutive physical properties are those of optical rotation and the absorption of light, the former depending solely upon the arrangement of the atoms in the molecule.

Although, at the present time, the relations between the chemical structure of compounds and the magnitude of their dissociation constants cannot be expressed by simple rules, nevertheless, the study of the dissociation constants of compounds has brought to light many interesting regularities. In this chapter we shall attempt to show how the number and kind of atoms and groups which are present in the molecule, and how the mode of linkage of these atoms and groups, influence the value of the dissociation constant. Our discussion will necessarily be confined to organic compounds, for it is only here that we have an extensive knowledge of the structure of the ions; and to acids and bases in particular, since these electrolytes obey the dilution law.

**The Influence of the Methyl Group.** The substitution of a hydrogen atom of an organic acid by a methyl group is invariably attended by a change in the value of the dissociation constant of the acid. When the substitution is made in the lowest member of an homologous series of acids, a large decrease in the value of the dissociation constant, and therefore in the strength of the acid, is brought about. For subsequent substitutions, the decrease in the value of the dissociation constant gradually becomes smaller, and, ultimately, a slight increase in the value may result. The influence of the substitution of the methyl group in acids of the formic acid series is illustrated by Table LXXXIX.<sup>1</sup> It will be observed that, though the substitution of the methyl group for a

<sup>1</sup> Except where otherwise stated, the values given in this chapter for dissociation constants have been taken from Schudder's *Conductivity and Ionization Constants of Organic Compounds*, and refer to 25°.

hydrogen atom in formic acid brings about a tenfold decrease in the value of the dissociation constant, the decrease effected by the next substitution is less than one-fourth.

TABLE LXXXIX

## DISSOCIATION CONSTANTS OF HOMOLOGOUS ACIDS

Acid	Formula	$K \times 10^5$
Formic	$\text{HCO}_2\text{H}$	21.4
Acetic	$\text{CH}_3 \cdot \text{CO}_2\text{H}$	1.8
Propionic	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$	1.34
Butyric	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$	1.49
Valeric	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$	1.61
Caproic	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$	1.45

As would be expected, when the methyl group replaces a hydrogen atom in an amine, the influence of the substitution on the value of the dissociation constant is the reverse of that in the case of acids. It will be seen from Table XC that the introduction of the methyl group strengthens the basic character of the amine, and, as with acids, the first group introduced brings about the greatest change in the value of the dissociation constant. It may be stated that, in general, the influence on the value of the dissociation constant of the substitution of different groups in bases is the reverse of that in acids. Any substituent that increases the strength of an acid will decrease the strength of a base, and *vice versa*.

TABLE XC

## DISSOCIATION CONSTANTS OF HOMOLOGOUS BASES

Base	Formula	$K \times 10^5$
Ammonium hydroxide	$\text{HNH}_4\text{O}$	2.3
Methylamine	$\text{CH}_3\text{NH}_4\text{O}$	50.0
Ethylamine	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{NH}_4\text{O}$	56.0
Propylamine	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_4\text{O}$	47.0

The dissociation constants of isomeric acids have nearly the same value. However, the dissociation constant of aliphatic acids often increases as the normal chain is shortened, although a continued shortening of the chain is sometimes accompanied by a slight decrease in the value of the constant (Table XCI).

In an investigation of the alkyl-substituted succinic acids, Bone and Spanking<sup>1</sup> showed that the nature of the substituted radical exerts a characteristic influence on the value of the dissociation constant. They

<sup>1</sup> *J. Chem. Soc.*, **77**, 1298 (1900).

observed that, when the substituted radical was normal, the dissociation constants of both the *cis* and *trans* derivatives increased with the number of atoms in the radical; but when, on the other hand, the substituent was

TABLE XCI

## DISSOCIATION CONSTANTS OF ISOMERIC ACIDS

Acid	Formula	$K \times 10^5$
Normal valeric	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$	1.6
Isovaleric	$\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{CH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H} \\ \diagdown \\ \text{CH}_3 \end{array}$	1.7
Methylethylacetic	$\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{CH} \cdot \text{CO}_2\text{H} \\ \diagdown \\ \text{CH}_3 \cdot \text{CH}_2 \end{array}$	1.69
Normal caproic	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$	1.46
Isocaproic	$\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H} \\ \diagdown \\ \text{CH}_3 \end{array}$	1.57
Diethylacetic	$\begin{array}{c} \text{CH}_3 \cdot \text{CH}_2 \\ \diagup \\ \text{CH} \cdot \text{CO}_2\text{H} \\ \diagdown \\ \text{CH}_3 \cdot \text{CH}_2 \end{array}$	2.03

an *iso* radical, the dissociation constant of the *trans* derivatives decreased and that of the *cis* derivatives increased with the number of atoms in the radical.

In a narrow sense, the dissociation constants of isomeric amines of the same degree of saturation exhibit a small, but noticeable, difference.

TABLE XCII

## DISSOCIATION CONSTANTS OF METAMERIC BASES

Base	Formula	$K \times 10^2$
Ethylamine	$\text{C}_2\text{H}_5 \cdot \text{NH}_3(\text{OH})$	0.056
Dimethylamine	$(\text{CH}_3)_2\text{NH}_2(\text{OH})$	0.074
Propylamine	$\text{C}_3\text{H}_7 \cdot \text{NH}_3(\text{OH})$	0.047
Trimethylamine	$(\text{CH}_3)_3 \cdot \text{N}(\text{OH})$	0.0074
Isobutylamine	$\text{C}_4\text{H}_9 \cdot \text{NH}_3(\text{OH})$	0.031
Diethylamine	$(\text{C}_2\text{H}_5)_2 \cdot \text{NH}_2(\text{OH})$	0.126
Tetramethylammonium hydroxide	$(\text{CH}_3)_4 \cdot \text{N}(\text{OH})$	As strong as NaOH
Diisobutylamine	$(\text{C}_4\text{H}_9)_2 \cdot \text{NH}_2(\text{OH})$	0.048
Tetraethylammonium hydroxide	$(\text{C}_2\text{H}_5)_4 \cdot \text{N}(\text{OH})$	As strong as NaOH

When the methyl group is in the  $\beta$ -position, the base is weaker than when it is in the  $\alpha$ -position. In the metameric amines the influence of constitution is sometimes most marked. The secondary aliphatic amines are stronger bases than their primary and tertiary metamers; on the other hand, the primary, secondary, and tertiary amines are all very much weaker bases than the metameric quaternary bases, as is shown in Table XCII.

**The Influence of the Amino Group.** As might be expected from the strongly positive nature of this group, its substitution in organic acids produces a decided weakening of the acid character. Thus, for example, although the dissociation constants of the sulphonic acids are so high as to make their exact determination difficult, those of the aminosulphonic acids lie within the limits of measurement. With acids of average strength, the dissociation constants are greatly reduced by the introduction of the amino group. For instance, aminoacetic acid is 100,000 times as weak an acid as acetic acid, and aminomalonic acid is just half as strong as malonic acid.

**The Influence of Halogens and Cyanogen.** In accordance with their negative character, the replacement of the hydrogen of organic acids by the halogens or the cyanogen group produces a marked increase in the value of the dissociation constant, and, in successive substitutions, the first step, as usual, gives rise to the largest increase. This behavior is illustrated in Table XCIII.

TABLE XCIII  
DISSOCIATION CONSTANTS OF HALOGEN ACIDS

Acid	Formula	$K \times 10^5$
Acetic	$\text{CH}_3 \cdot \text{CO}_2\text{H}$	1.8
Monochloroacetic	$\text{CH}_2\text{Cl} \cdot \text{CO}_2\text{H}$	155
Dichloroacetic	$\text{CHCl}_2 \cdot \text{CO}_2\text{H}$	5140
Trichloroacetic	$\text{CCl}_3 \cdot \text{CO}_2\text{H}$	About 120,000
Cyanacetic	$\text{CH}_2\text{CN} \cdot \text{CO}_2\text{H}$	138
Benzoic	$\text{C}_6\text{H}_5 \cdot \text{CO}_2\text{H}$	6.6
<i>o</i> -Chlorobenzoic	$\text{C}_6\text{H}_4\text{Cl} \cdot \text{CO}_2\text{H}$	132.0
<i>o</i> -Bromobenzoic	$\text{C}_6\text{H}_4\text{Br} \cdot \text{CO}_2\text{H}$	145.0
<i>o</i> -Iodobenzoic	$\text{C}_6\text{H}_4\text{I} \cdot \text{CO}_2\text{H}$	132.0

**The Influence of Hydroxyl, Nitro and Carboxyl Groups.** Like the halogens, the replacement of a hydrogen atom of an organic acid by the hydroxyl, nitro, or carboxyl group increases the value of the dissociation constant of the acid. The increase is greater, the nearer the substituting group stands to the carboxyl group of the acid, as is shown by Table XCIV.

TABLE XCIV

## DISSOCIATION CONSTANTS OF SUBSTITUTED ACIDS

Acid	Formula	$K \times 10^5$
<i>Substitution of OH</i>		
Acetic	$\text{CH}_3 \cdot \text{CO}_2\text{H}$	1.8
Glycollic	$\text{CH}_2\text{OH} \cdot \text{CO}_2\text{H}$	15.2
Glyoxalic	$\text{CH}(\text{OH})_2 \cdot \text{CO}_2\text{H}$	47
Benzoic	$\text{C}_6\text{H}_5 \cdot \text{CO}_2\text{H}$	6.6
<i>p</i> -Oxybenzoic	$\text{C}_6\text{H}_4(\text{OH}) \cdot \text{CO}_2\text{H}$ (1 : 4)	2.86
<i>m</i> -Oxybenzoic	$\text{C}_6\text{H}_4(\text{OH}) \cdot \text{CO}_2\text{H}$ (1 : 3)	8.33
<i>o</i> -Oxybenzoic	$\text{C}_6\text{H}_4(\text{OH}) \cdot \text{CO}_2\text{H}$ (1 : 2)	105.0
<i>Substitution of NO<sub>2</sub></i>		
Benzoic	$\text{C}_6\text{H}_5 \cdot \text{CO}_2\text{H}$	6.6
<i>p</i> -Nitrobenzoic	$\text{C}_6\text{H}_4(\text{NO}_2) \cdot \text{CO}_2\text{H}$ (1 : 4)	40.1
<i>m</i> -Nitrobenzoic	$\text{C}_6\text{H}_4(\text{NO}_2) \cdot \text{CO}_2\text{H}$ (1 : 3)	34.8
<i>o</i> -Nitrobenzoic	$\text{C}_6\text{H}_4(\text{NO}_2) \cdot \text{CO}_2\text{H}$ (1 : 2)	615.0
<i>Substitution of CO<sub>2</sub>H</i>		
Benzoic	$\text{C}_6\text{H}_5 \cdot \text{CO}_2\text{H}$	6.6
<i>p</i> -Phthalic	$\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ (1 : 4)	15.0
<i>m</i> -Phthalic	$\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ (1 : 3)	29.0
<i>o</i> -Phthalic	$\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ (1 : 2)	121.0

On *a priori* grounds, it is obvious that the mutual influence of two carboxyl groups in the molecule must increase the tendency to dissociate, and that the magnitude of this mutual reinforcement must vary inversely as the distance between the two carboxyl groups. Hence, the value of the dissociation constant of dibasic acids should decrease as the number of atoms between the two carboxyl groups increases. That this is so is shown by Table XCV.

TABLE XCV

## DISSOCIATION CONSTANTS OF DIBASIC ACIDS

Acid	Formula	$K \times 10^5$
Oxalic	$\text{CO}_2\text{H} \cdot \text{CO}_2\text{H}$	About 10,000
Malonic	$\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$	163
Succinic	$\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$	6.8
Glutaric	$\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$	4.75
Adipic	$\text{CO}_2\text{H} \cdot (\text{CH}_2)_4 \cdot \text{CO}_2\text{H}$	3.65
Pimelic	$\text{CO}_2\text{H} \cdot (\text{CH}_2)_5 \cdot \text{CO}_2\text{H}$	3.4
Suberic	$\text{CO}_2\text{H} \cdot (\text{CH}_2)_6 \cdot \text{CO}_2\text{H}$	2.96
Sebacic	$\text{CO}_2\text{H} \cdot (\text{CH}_2)_7 \cdot \text{CO}_2\text{H}$	2.76



**The Influence of Linkage.** The mode of linkage of the carbon atoms in an organic acid exerts a marked influence on the value of the dissociation constant. In general, the greater the degree of unsaturation, the greater is the strength of the acid. This is illustrated in Table XCVI.

TABLE XCVI

## DISSOCIATION CONSTANTS OF UNSATURATED ACIDS

Acid	Formula	$K \times 10^5$
Propionic	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$	1.34
Acrylic	$\text{CH}_2 : \text{CH} \cdot \text{CO}_2\text{H}$	5.6
Butyric	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$	1.6
Crotonic	$\text{CH}_3 \cdot \text{CH} : \text{CH} \cdot \text{CO}_2\text{H}$	2.15
Tetrollic	$\text{CH}_3 \cdot \text{C} : \text{C} \cdot \text{CO}_2\text{H}$	250

**Wegscheider's Summary for Acids.** From the results of his own and other measurements, Wegscheider<sup>1</sup> compiled a table of the factors which represent the influence of the various substituting atoms or groups on the dissociation constant of saturated aliphatic and aromatic monobasic acids. These numbers are the factors by which the value of the dissociation constant of an acid must be multiplied, in order to obtain the value of the dissociation constant of the acid derived by the substitution of the atoms or groups to which the factors refer. These factors are given in Table XCVII. If the table were complete, it would be possible to calculate the dissociation constants of all other acids from the values of the dissociation constants of the simple carboxylic acids.

It will be observed that the factors for the halogens decrease, generally, from chlorine to iodine, independently of the position in which the atoms are substituted. For a negative substituting group, the factor decreases rapidly with the change of the group from the  $\alpha$ - to the  $\beta$ -position, and then less rapidly to the  $\delta$ -position. The values given in the table show that the influence of either the methyl or ethyl group in the  $\alpha$ -position is greatest when it substitutes a hydrogen atom of a methylene group ( $\text{CH}_2$ ) and least when the substitution is made in a methenyl group ( $\text{CH}$ ). In the  $\alpha$ -position a methyl or ethyl group has a negative influence (i.e., increases the value of the dissociation constant), which gradually changes to positive as the distance between the carboxyl group and the position of substitution increases. The influence of the methyl group in aromatic acids varies in a similar manner, becoming positive in the *meta* and *para* positions. The influence of this group in the *ortho* position

<sup>1</sup> *Monatsh.*, **23**, 289 (1902).

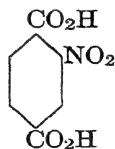
TABLE XCVII

FACTORS EXPRESSING THE INFLUENCE OF SUBSTITUENTS ON THE  
DISSOCIATION CONSTANTS OF ACIDS

Substituent	Position in Which the Atom or Group is Substituted in:						
	The Chain of a Saturated Fatty Acid				An Aromatic Acid		
	$\alpha$	$\beta$	$\gamma$	$\delta$	<i>o</i>	<i>m</i>	<i>p</i>
Cl	90	6.2	2.0	1.27	22	2.58	1.55
Br	76	7.3	1.76	1.19	24	2.28	....
I	42	6.72	1.53	1.06	....	....	....
NO <sub>2</sub>	.....	12.5	....	....	103	5.75	6.60
OH	8.4	2.31	....	....	17	1.45	0.48
CH <sub>3</sub>	$\left\{ \begin{array}{l} 0.74 \\ 1.10 \\ 0.62 \end{array} \right\}$	1.12	1.00	0.90	2.0	0.86	0.85
C <sub>2</sub> H <sub>5</sub>	$\left\{ \begin{array}{l} 0.83 \\ 1.31 \\ 0.66 \end{array} \right\}$	1.20	0.98	0.81	....	....	....
CO <sub>2</sub> H	34	2.41	1.67	1.2	10.2	2.39	2.62
CO <sub>2</sub> CH <sub>3</sub>	.....	2.4	....	....	11.0	....	2.8
CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	27	2.25	....	....	9.2	....	....

resembles that in the  $\beta$ -position, and the influence in the *meta* and *para* positions is analogous to that in the  $\gamma$ -position. The nature of the influence of the hydroxyl and methoxy groups is similar. Since in compiling the table it was not possible to take small differences in constitution into account, calculations based on the factors are only approximate.

In order to illustrate the practical value of the factors given in Table XCVII, the calculation of the dissociation constant of 2-nitro-*p*-phthalic acid is given. This acid may be regarded as benzoic acid, in which a nitro group has been substituted in a position *ortho* to the carboxyl group, and a carboxyl group in a position *para* to the first carboxyl group:



For benzoic acid	$K = 6.6 \times 10^{-5}$
The factor for the <i>ortho</i> substitution of $\text{NO}_2$	103
The factor for the <i>para</i> substitution of $\text{CO}_2\text{H}$	2.62
Therefore, for $\text{CO}_2\text{H}$ , <i>ortho</i> to $\text{NO}_2$	$K = 6.6 \times 10^{-5} \times 103 \times 2.62$ $= 1.78 \times 10^{-2}$
The factor for the <i>meta</i> substitution of $\text{NO}_2$	$= 5.75$
The factor for the <i>para</i> substitution of $\text{CO}_2\text{H}$	$= 2.62$
Therefore, for $\text{CO}_2\text{H}$ , <i>meta</i> to $\text{NO}_2$	$K = 6.6 \times 10^{-5} \times 5.75 \times 2.62$
For 2-nitro- <i>p</i> -phthalic acid	$K = 1.78 \times 10^{-2} + 0.099 \times 10^{-2}$ $= 1.879 \times 10^{-2}$
As found by experiment	$K = 1.87 \times 10^{-2}$

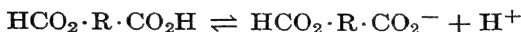
**The Dissociation of Polybasic Acids.** If a hydrogen atom dissociates from each carboxyl group of the molecules of a polybasic acid, evidently the dissociation equilibrium of the acid cannot be expressed by the dilution law. Since the organic polybasic acids actually do obey this law over a wide range of concentration, we must conclude that hydrogen atoms dissociate from only one carboxyl group, and that their dissociation from the other groups takes place with considerably greater difficulty than from the first. That hydrogen atoms do dissociate, eventually, from other groups than the first is shown by the failure of the dilution law at low concentrations (see Table XCVIII).

TABLE XCVIII

## THE SECOND DISSOCIATION OF DIBASIC ACIDS

Acid	Formula	Dilution at Which Second Dissociation Sets in, $V$	Degree of Dissociation of First $\text{CO}_2\text{H}$ Group at $V$
Tartaric	$\text{C}_2\text{H}_2(\text{OH})_2(\text{CO}_2\text{H})_2$	128	0.30-0.40
Malonic	$\text{CH}_2(\text{CO}_2\text{H})_2$	256	0.46-0.58
Tartronic	$\text{CH}(\text{OH})(\text{CO}_2\text{H})_2$	256	0.40-0.52
$\alpha$ -Nitrophthalic	$\text{C}_6\text{H}_3\text{NO}_2(\text{CO}_2\text{H})_2$	256	0.80-0.89
Fumaric	$\text{HO}_2\text{C} \cdot \text{C}_2\text{H}_2 \cdot \text{CO}_2\text{H}$	256	0.40-0.50
Malic	$\text{C}_2\text{H}_3(\text{OH})\text{CO}_2\text{H}$	1024	0.47-0.60
<i>o</i> -Phthalic	$\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$	1024	0.66-0.78
Maleic	$\text{C}_2\text{H}_2(\text{CO}_2\text{H})_2$	> 1024	> 0.93

The retardation of the dissociation of the second carboxyl group of a dibasic acid has been attributed <sup>1</sup> to the action of the negative charge of the anion acquired by the dissociation



The presence of this charge is supposed to make it more difficult for the

<sup>1</sup> Cf. Ostwald, *Z. physik. Chem.*, **3**, 186, 280 (1889).

anion to acquire another negative charge by the dissociation of the second carboxyl group, owing to the repulsion of like and the attraction of unlike electric charges. In a tribasic acid, the dissociation of hydrogen ions from two carboxyl groups would make it still more difficult for the third group to part with a hydrogen ion. If this view is correct, we should expect that the nearer, spatially, the carboxyl groups are to one another, the higher would be the dilution at which the second (or third) dissociation sets in and, therefore, at which the dilution law fails. That this is actually true is illustrated by the data given in Table XCVIII for a number of dibasic acids. The influence of the proximity of the carboxyl groups is strikingly shown by the isomeric acids, fumaric and maleic: with fumaric the second dissociation sets in at a dilution of 256 liters; with maleic, in which the carboxyl groups are adjacent, this dissociation does not begin even at a dilution of 1024 liters.

**The Dissociation of Dibasic Acids.** The dissociation of dibasic acids takes place in two stages:



and



In accordance with the law of mass action, the dissociation constant of the first step is given by the expression

$$K_1 = \frac{[\text{H}^+][\text{HA}^-]}{[\text{H}_2\text{A}]} \quad (1)$$

and that of the second by

$$K_2 = \frac{[\text{H}^+][\text{A}^{--}]}{[\text{HA}^-]} \quad (2)$$

Provided that the concentrations employed are not too low, the first dissociation constant ( $K_1$ ) of a dibasic acid may be obtained from conductance measurements by means of the dilution law. In order to derive an expression by which the second dissociation constant ( $K_2$ ) may be calculated, let us consider the dissociation of an acid salt,  $\text{MAH}$ , having a concentration  $c$ . This salt dissociates as follows:



and



The ions  $\text{H}^+$  and  $\text{HA}^-$  recombine to a certain extent to form undissociated molecules of the dibasic acid



Since the negative ions,  $A^{--}$ , are produced by the reaction



and the direct dissociation of the  $HA^-$  ion, it is evident that

$$[A^{--}] = [H^+] + [H_2A] \quad (3)$$

and

$$[A^{--}] + [HA^-] + [H_2A] = c \quad (4)$$

when the concentrations of the acid and neutral salt are negligible. (This is true in dilute solutions.) On combining equations 3 and 4, we obtain

$$[HA^-] = c + [H^+] - 2[A^{--}] \quad (5)$$

From equation 2 it follows that

$$[HA^-] = \frac{[H^+][A^{--}]}{K_2} = c + [H^+] - 2[A^{--}]$$

or

$$[H^+][A^{--}] = K_2c + K_2[H^+] - 2K_2[A^{--}] \quad (6)$$

On combining equations 1 and 3, we get

$$[HA^-] = \frac{K_1[A^{--}] - K_1[H^+]}{[H^+]} \quad (7)$$

On substituting for  $[HA^-]$  the value obtained from equation 2, we have

$$\frac{[H^+][A^{--}]}{K_2} = \frac{K_1[A^{--}] - K_1[H^+]}{[H^+]}$$

whence

$$[A^{--}] = \frac{K_1K_2[H^+]}{K_1K_2 - [H^+]^2} \quad (8)$$

On substituting this value of  $[A^{--}]$  in equation 6, we obtain, on simplifying,

$$K_2 = \frac{(K_1 + c + [H^+])[H^+]^2}{K_1(c - [H^+])} \quad (9)$$

or, if the concentration of the hydrogen ions is negligible (less than 1 per cent), we may write

$$K_2 = \frac{(K_1 + c)[H^+]^2}{K_1c} \quad (10)$$

Since  $c$  is known and  $K_1$  and  $[H^+]$  may be determined experimentally,  $K_2$  can be calculated.

Equations 9 and 10, first derived by Noyes,<sup>1</sup> were employed by Smith<sup>2</sup> to calculate the second dissociation constant of a number of dibasic acids. Smith determined the hydrogen-ion concentration of solutions of the acid salts, by means of measurements of the rate of the inversion of cane sugar in the presence of the salts (see pp. 350 and 380). A number of the values obtained by him are given in Table XCIX.

TABLE XCIX

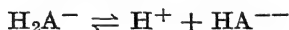
FIRST AND SECOND DISSOCIATION CONSTANTS OF DIBASIC ACIDS

Acid	$K_1 \times 10^6$	$K_2 \times 10^6$
Malonic	1,580	1.0
Succinic	66.5	2.3
Glutaric	43.7	2.7
Adipic	37.6	2.4
Maleic	11,700	0.39
Fumaric	930	18.0
Citraconic	3,400	0.24
Mesaconic	790	6.8
Tartaric	970	59.0
Malic	399	8.3
Dipropylmalonic	11,200	0.05
Methylethylmalonic	1,610	0.17

These numbers for the second dissociation constant are not strictly accurate, since the values used for  $K_1$  and  $[H^+]$  correspond to 25° and 100°, respectively.

Other expressions and methods for the calculation of the second dissociation constant of dibasic acids have been derived and employed by McCoy,<sup>3</sup> Chandler,<sup>4</sup> Drucker,<sup>5</sup> Duboux,<sup>6</sup> Larsson,<sup>7</sup> and Paul.<sup>8</sup>

**The Dissociation of Tribasic Acids.** In tribasic acids, three stages of dissociation are possible:



<sup>1</sup> *Z. physik. Chem.*, **11**, 495 (1893).

<sup>2</sup> *Ibid.*, **25**, 193 (1898).

<sup>3</sup> *J. Am. Chem. Soc.*, **30**, 688 (1908).

<sup>4</sup> *Ibid.*, **30**, 694 (1908).

<sup>5</sup> *Z. Elektrochem.*, **26**, 364 (1920); *Z. physik. Chem.*, **96**, 381 (1920).

<sup>6</sup> *J. chim. phys.*, **19**, 179 (1921).

<sup>7</sup> *Z. anorg. Chem.*, **125**, 281 (1923).

<sup>8</sup> *Z. physik. Chem.*, **110**, 417 (1924).

Very few determinations have been made of the dissociation constants of acids of this type. The following approximate values<sup>1</sup> have been obtained for the constants of citric acid:

$$K_1 = \frac{[\text{H}^+][\text{H}_2\text{A}^-]}{[\text{H}_3\text{A}]} = 0.082 \times 10^{-5}$$

$$K_2 = \frac{[\text{H}^+][\text{HA}^{--}]}{[\text{H}_2\text{A}^-]} = 0.0032 \times 10^{-5}$$

$$K_3 = \frac{[\text{H}^+][\text{A}^{---}]}{[\text{HA}^{--}]} = 0.00007 \times 10^{-5}$$

**Summary.** The influence of substituents on the strength of organic acids and bases, as measured by the magnitude of their dissociation constants, has been discussed. The strength of an acid is increased by the substitution of a methyl hydrogen by an electronegative group and decreased by the substitution of a methyl hydrogen by an electropositive group. Substituents which increase the strength of acids decrease the strength of bases, and *vice versa*. The change in strength, which is greater the nearer, spatially, the substituent stands to the dissociating group, may be attributed to a displacement of the electrons in the molecule. Thus in acetic acid, "the substitution of one methyl hydrogen by chlorine produces a greater pull upon the electrons of the methyl carbon, and this causes a displacement which seems to occur throughout the molecule, finally pulling the electrons away from the hydrogen [of the carboxyl group] and permitting a greater dissociation."<sup>2</sup>

Dibasic acids obey the dilution law at higher concentrations, indicating that hydrogen dissociates from only one of the carboxyl groups. That both carboxyl groups can dissociate is shown by the failure of the dilution law at low concentrations. The retardation of the dissociation of the second carboxyl group is due to the influence which the two carboxyl groups exert on one another. This influence and the dilution at which the dilution law first ceases to hold are greater the nearer, spatially, the carboxyl groups are in the molecule.

The dissociation of dibasic acids is governed by two and that of tribasic acids by three dissociation constants: one for each stage of dissociation. The first dissociation constant is usually much larger than the others.

<sup>1</sup>Smith *loc. cit.*; cf. Hastings and van Slyke, *J. Biol. Chem.*, **53**, 269 (1922); Adell, *Z. physik. Chem.*, **A187**, 66 (1941).

<sup>2</sup>Lewis, *Valence and Structure of Atoms and Molecules*, p. 139, 1923.

## PROBLEMS

(Data necessary for the solution of Problems 1 to 4 will be found in Table XCVII.)

1. Given that the dissociation constant of benzoic acid is  $6.6 \times 10^{-5}$  at  $25^\circ$ , calculate the dissociation constant of *meta*-methylbenzoic acid.

2. Given that the dissociation constant of acetic acid is  $1.8 \times 10^{-5}$  at  $25^\circ$ , calculate the dissociation constants of the chloracetic acids.

3. Regarding isobutyric acid as acetic acid in which first a methyl hydrogen is substituted by a methyl group, and then a second methyl group is substituted in the resulting methylene group, calculate the dissociation constant of the acid, using for the dissociation constant of acetic acid the value given in the preceding problem.

4. Calculate the dissociation constant of *meta*-phthalic acid, being given that the dissociation constant of benzoic acid is  $6.6 \times 10^{-5}$ , at  $25^\circ$ .

5. At a dilution of 128 liters, the concentration of the hydrogen ions in a solution of an acid salt of succinic acid is  $1.2 \times 10^{-5}$  gram ion per liter. Given that the first dissociation constant of the acid is  $66.5 \times 10^{-6}$ , calculate the second dissociation constant.



## CHAPTER XVII

### HOMOGENEOUS EQUILIBRIA

**Mixtures of Two Electrolytes with a Mutual Ion.** We have already seen that electrolytic dissociation of a weak electrolyte is but a special type of reversible reaction; and that for the dissociation



the equilibrium, or dissociation, constant is given by the expression

$$K = \frac{[\text{M}^+][\text{A}^-]}{[\text{MA}]} \quad (1)$$

If, to a solution of the electrolyte MA, another having a common ion (M'A or MA') is added, the numerator of the right-hand member of equation 1 will be increased. Since the value of the dissociation constant  $K$  is independent of the concentrations of the ions and the undissociated molecules, it follows that the value of the numerator must decrease and that of the denominator must increase, until the value of the ratio becomes equal to  $K$ . This change is brought about by the union of the ions  $\text{M}^+$  and  $\text{A}^-$  to form undissociated molecules, MA. Evidently, a similar change must take place in the dissociation of the second electrolyte. Hence, *on mixing solutions of two electrolytes having a common ion the degrees of dissociation of the electrolytes are mutually decreased*. This behavior was first quantitatively studied by Arrhenius.<sup>1</sup>

In order to ascertain the extent to which the dissociation of each electrolyte is repressed by the presence of the other, let us consider a solution containing two weak uniunivalent acids  $\text{HA}_1$  and  $\text{HA}_2$ , having concentrations  $c_1$  and  $c_2$ , respectively. Further, let the respective degrees of dissociation of the acids in the mixture be  $\alpha_1$  and  $\alpha_2$ , and in pure solutions of the same concentrations,  $\beta_1$  and  $\beta_2$ .

The dissociation constants of the two acids are given by the expressions<sup>2</sup>

$$K_1 = [\text{H}^+] \frac{\alpha_1}{(1 - \alpha_1)} \quad (2)$$

<sup>1</sup> *Wied. Ann.*, **30**, 51 (1887); *Z. physik. Chem.*, **2**, 284 (1888).

<sup>2</sup> The symbols  $K_1$  and  $K_2$  will be employed to denote the dissociation constants of two acids, as well as the first and second dissociation constants of a dibasic acid.

and

$$K_2 = [\text{H}^+] \frac{\alpha_2}{(1 - \alpha_2)} \quad (3)$$

where  $[\text{H}^+]$  is the hydrogen-ion concentration in the mixture. On combining these equations, we obtain

$$\frac{K_1}{K_2} = \frac{\alpha_1}{(1 - \alpha_1)} \cdot \frac{(1 - \alpha_2)}{\alpha_2} \quad (4)$$

Since the degrees of dissociation of weak electrolytes are small, and since in a mixture of weak electrolytes containing a mutual ion the degrees of dissociation are still smaller, the approximation

$$1 - \alpha_1 = 1 - \alpha_2 = 1 \quad (5)$$

suffices, and we may write

$$\frac{\alpha_2}{\alpha_1} = \frac{K_2}{K_1} \quad (6)$$

Since

$$K_1 = \frac{\beta_1^2 c_1}{(1 - \beta_1)} \quad (7)$$

and also

$$K_1 = \frac{\alpha_1}{(1 - \alpha_1)} (\alpha_1 c_1 + \alpha_2 c_2) \quad (8)$$

it follows that

$$\begin{aligned} \frac{\beta_1^2 c_1}{(1 - \beta_1)} &= \frac{\alpha_1}{(1 - \alpha_1)} (\alpha_1 c_1 + \alpha_2 c_2) \\ &= \frac{\alpha_1^2}{(1 - \alpha_1)} \left( c_1 + \frac{\alpha_2}{\alpha_1} c_2 \right) \end{aligned} \quad (9)$$

On substituting in this equation the value of  $\alpha_2/\alpha_1$  given in equation 6, we obtain

$$\frac{\beta_1^2 c_1}{(1 - \beta_1)} = \frac{\alpha_1^2}{(1 - \alpha_1)} \left( c_1 + \frac{K_2}{K_1} c_2 \right) \quad (10)$$

On making the approximation

$$1 - \beta_1 = 1 - \alpha_1 = 1 \quad (11)$$

equation 10 reduces to

$$\begin{aligned}\beta_1^2 c_1 &= \alpha_1^2 \left( c_1 + \frac{K_2}{K_1} c_2 \right) \\ &= \alpha_1^2 c_1 \left( 1 + \frac{K_2}{K_1} \cdot \frac{c_2}{c_1} \right)\end{aligned}$$

or

$$\frac{\beta_1}{\alpha_1} = \sqrt{1 + \frac{K_2}{K_1} \cdot \frac{c_2}{c_1}} \quad (12)$$

Equation 12 represents the ratio in which the degree of dissociation of an acid,  $\text{HA}_1$ , at a concentration,  $c_1$ , is repressed by the addition of  $c_2$  moles per liter of an acid,  $\text{HA}_2$ . The extent to which the degree of dissociation of the acid  $\text{HA}_2$  is decreased, owing to the presence of  $\text{HA}_1$ , is given by the expression

$$\frac{\beta_2}{\alpha_2} = \sqrt{1 + \frac{K_1}{K_2} \cdot \frac{c_1}{c_2}} \quad (12a)$$

On combining equations 12 and 12a, we obtain the general expression

$$\frac{\beta_1 : \alpha_1}{\beta_2 : \alpha_2} = \sqrt{\frac{1 + \frac{K_2}{K_1} \cdot \frac{c_2}{c_1}}{1 + \frac{K_1}{K_2} \cdot \frac{c_1}{c_2}}} = \sqrt{\frac{K_2 c_2}{K_1 c_1}} \quad (13)$$

In order to ascertain the magnitude of the repressions of the degrees of dissociation which occur on mixing two electrolytes having a mutual ion, let us consider an aqueous solution containing one mole of lactic acid ( $K_1 = 1.4 \times 10^{-4}$ ) and one mole of trichloroacetic acid ( $K_2 = 46.0 \times 10^{-4}$ ) per liter. In a solution of pure lactic acid containing one mole per liter, the degree of dissociation is

$$\beta_1 = \sqrt{\frac{K_1}{c_1}} = \sqrt{1.4 \times 10^{-4}} = 0.01183$$

Hence, the degree of dissociation of lactic acid in the mixture is

$$\alpha_1 = \frac{0.01183}{\sqrt{1 + \frac{46}{1.4}}} = 0.002023$$

That is, the dissociation of lactic acid is reduced from 1.183 per cent to 0.2023 per cent. On the other hand, the dissociation of the stronger trichloroacetic acid is reduced only from 6.783 per cent to 6.682 per cent.

It is evident, therefore, that the degree of dissociation of the weaker acid is influenced to a much greater extent than that of the stronger acid.

**The Influence of Neutral Salts on the Dissociation of Weak Acids and Bases.** Since neutral salts are largely dissociated, even at concentrations as high as normal, it is evident that the degree of dissociation of a weak acid or base must be practically negligible in the presence of its neutral salts. If a weak acid, HA, having a concentration  $c_1$ , is present in solution with one of its neutral salts, MA, having a concentration  $c_2$ , then the dissociation constant of the acid will be given by the expression

$$K = \frac{\alpha_1}{(1 - \alpha_1)} (\alpha_1 c_1 + \alpha_2 c_2)$$

where  $\alpha_1$  and  $\alpha_2$  are the degrees of dissociation of the acid and the salt, respectively. Since the salt is highly dissociated and, in consequence, the degree of dissociation of the acid is very small, we may make the approximation

$$1 - \alpha_1 = \alpha_2 = 1 \quad (14)$$

Hence

$$K = \alpha_1^2 c_1 + \alpha_1 c_2 \quad (15)$$

If  $c_1$  and  $c_2$  are of the same order of magnitude, we may make the further approximation

$$K = \alpha_1 c_2$$

or

$$\alpha_1 = \frac{K}{c_2} \quad (16)$$

That is, the degree of dissociation of a weak acid or weak base, in the presence of one of its neutral salts, is approximately inversely proportional to the concentration of the salt.

In a solution containing 1 normal ammonium hydroxide and 1 normal ammonium chloride, the degree of dissociation of the base, then, is

$$\alpha_1 = \frac{0.000023}{1} = 0.0023 \text{ per cent}$$

whereas the degree of dissociation of ammonium hydroxide in a pure solution of the same concentration is

$$\beta_1 = \sqrt{\frac{0.000023}{1}} = 0.48 \text{ per cent}$$

It has been mentioned (p. 44) that one of the characteristics of the hydrogen ion is its ability to accelerate, catalytically, the inversion of

cane sugar. Study of this property has shown that the rate at which the inversion of the sugar takes place is directly proportional to the hydrogen-ion concentration. Arrhenius<sup>1</sup> employed this behavior to determine the influence of their sodium salts upon the degrees of dissociation of formic and acetic acids. His results (Table C) show that the velocity

TABLE C

INVERSION OF CANE SUGAR AT 54° IN THE PRESENCE OF ACIDS AND THEIR NEUTRAL SALTS

Acid and Salt	Velocity Constant $k \times 10^3$	
	Observed	Calculated
0.25 <i>N</i> HCO <sub>2</sub> H + 0.000 <i>N</i> HCO <sub>2</sub> Na	2.55	2.54
0.25 <i>N</i> HCO <sub>2</sub> H + 0.025 <i>N</i> HCO <sub>2</sub> Na	0.72	0.75
0.25 <i>N</i> HCO <sub>2</sub> H + 0.1 <i>N</i> HCO <sub>2</sub> Na	0.24	0.24
0.25 <i>N</i> HCO <sub>2</sub> H + 0.25 <i>N</i> HCO <sub>2</sub> Na	0.118	0.117
0.25 <i>N</i> CH <sub>3</sub> CO <sub>2</sub> H + 0.0000 <i>N</i> CH <sub>3</sub> CO <sub>2</sub> Na	0.75	0.74
0.25 <i>N</i> CH <sub>3</sub> CO <sub>2</sub> H + 0.0125 <i>N</i> CH <sub>3</sub> CO <sub>2</sub> Na	0.122	0.129
0.25 <i>N</i> CH <sub>3</sub> CO <sub>2</sub> H + 0.025 <i>N</i> CH <sub>3</sub> CO <sub>2</sub> Na	0.070	0.070
0.25 <i>N</i> CH <sub>3</sub> CO <sub>2</sub> H + 0.05 <i>N</i> CH <sub>3</sub> CO <sub>2</sub> Na	0.040	0.038
0.25 <i>N</i> CH <sub>3</sub> CO <sub>2</sub> H + 0.125 <i>N</i> CH <sub>3</sub> CO <sub>2</sub> Na	0.019	0.017
0.25 <i>N</i> CH <sub>3</sub> CO <sub>2</sub> H + 0.25 <i>N</i> CH <sub>3</sub> CO <sub>2</sub> Na	0.0105	0.0100

constant  $k$  (which is a measure of the rate of inversion) of the inversion of cane sugar by a mixture of either acid and its salt decreases as the ratio, salt : acid, increases, thus demonstrating that the presence of the salt actually causes a decrease in the dissociation of the acid, the inversion rate being proportional to the hydrogen-ion concentration.

In a mixture of two binary electrolytes of like strength (i.e.,  $K_1 = K_2$ ) which have a mutual ion and concentrations  $c_1$  and  $c_2$ , respectively, Nernst<sup>2</sup> showed that the degree of dissociation of each is equal to and of the same value as that which would correspond to each alone at the concentration ( $c_1 + c_2$ ).

**Explanations of Certain Chemical Phenomena.** Many well-known chemical phenomena can be explained by means of the theory of mixed electrolytes discussed in the preceding pages. For instance, the non-

<sup>1</sup> *Z. physik. Chem.*, **4**, 226 (1889); **5**, 7 (1890).

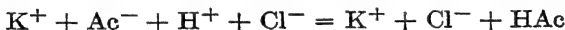
<sup>2</sup> *Ibid.*, **4**, 380 (1889).

precipitation of zinc by hydrogen sulphide in acid solution is due to the fact that the high hydrogen-ion concentration of the acid reduces the degree of dissociation of the hydrogen sulphide to such an extent that the concentration of the  $S^{--}$  ions is insufficient to form an appreciable amount of zinc sulphide (see also Chapter XXIII). Similarly, magnesium is not precipitated by ammonium hydroxide in the presence of ammonium salts.

Whenever two binary electrolytes are present in solution, their four ions may react to form the four possible undissociated substances, the amounts formed of each being governed by the equilibrium equations we have discussed. When all the four possible products are strong electrolytes, the ions react to but a negligible extent. However, ionic reactions occur when one of the possible products is a weak electrolyte, or a slightly soluble substance (the latter case will be considered in Chapter XXIII). For example, if we introduce potassium and acetate ions (potassium acetate) into a solution containing hydrogen and chlorine ions (hydrochloric acid), there is a great tendency for the acetate and hydrogen ions to combine to form undissociated acetic acid, for

$$K_{HAc} : \frac{[H^+][Ac^-]}{[HAc]} \quad 1.8 \times 10^{-5}$$

Since this ratio must always be satisfied, it is evident, therefore, that hydrogen and acetate ions must unite with one another to form undissociated molecules of acetic acid, and that this union must proceed until the concentrations of these ions are reduced, and the concentration of the undissociated molecules is increased, to such an extent that the product of the concentrations of the ions divided by the concentration of the undissociated molecules is equal to  $1.8 \times 10^{-5}$ . This results in the conversion of practically all the potassium acetate into acetic acid. The reaction which takes place in this case may be written



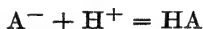
or, omitting those substances which occur on both sides of the equation, simply



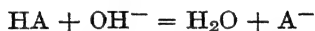
Similarly, when a solution of a strong base is added to a solution of a salt of a weak base, the weak base is "liberated."

**Buffer Solutions.** If to a liter of pure water 1 cc of 0.01 normal hydrochloric acid were added the hydrogen-ion concentration would increase from  $10^{-7}$  (see p. 361) to  $10^{-5}$ , while the addition of the same

quantity of 0.01 normal sodium hydroxide would bring about the same increase in the hydroxyl-ion concentration. On the other hand, if the solution of the acid or alkali were added to a liter of a solution of a weak acid, HA, and its salt, MA, the resulting change in the hydrogen-ion or hydroxyl-ion concentration would be scarcely appreciable. This results from the fact that increase in the concentration of hydrogen or hydroxyl ions on the addition of acid or alkali is opposed by the reaction



or



This power of certain solutions to resist change in hydrogen-ion or hydroxyl-ion concentration, on the addition of acids or alkalis, is known as **buffer action**, and solutions which exhibit this action are termed **buffer solutions**.

Buffer solutions evidently possess a reserve acidity or alkalinity. Since, in accordance with the law of mass action,

$$[H^{+}] = \frac{[HA]}{[A^{-}]} K_a$$

it follows, when

$$[H^{+}] = K_a$$

or

$$[A^{-}] = [HA]$$

that the reserve acidity and alkalinity of a buffer solution will be equal.

**Isohydric Solutions.** If solutions of two acids having the same hydrogen-ion concentration are mixed, no change takes place in the degree of dissociation of either. This is due to the fact that the value of  $[H^{+}]$  in the equation

$$K = \frac{[H^{+}][A^{-}]}{[HA]} \quad (17)$$

remains unchanged, while the values of  $[A^{-}]$  and  $[HA]$  for each acid are altered to the same extent. Solutions, containing a mutual ion, whose degrees of dissociation remain unchanged on mixing are called **isohydric solutions**.

In order to determine the conditions which must be fulfilled so that two solutions may be isohydric, let us consider a solution containing two weak uniunivalent acids,  $HA_1$  and  $HA_2$ , having, respectively, concentrations  $c_1$  and  $c_2$ , and degrees of dissociation  $\alpha_1$  and  $\alpha_2$ . From equations 2 and 3 it follows that

$$\frac{1}{\alpha_1} = 1 + \frac{[\text{H}^+]}{K_1} \quad (18)$$

and

$$\frac{1}{\alpha_2} = 1 + \frac{[\text{H}^+]}{K_2} \quad (19)$$

If  $c'_1$  and  $c'_2$  represent the concentrations of isohydric solutions of the pure acids, i.e., the concentrations of solutions of the pure acids having the degrees of dissociation  $\alpha_1$  and  $\alpha_2$ , then, since

$$K_1 = \frac{\alpha_1^2 c'_1}{(1 - \alpha_1)} \quad (20)$$

and

$$K_2 = \frac{\alpha_2^2 c'_2}{(1 - \alpha_2)} \quad (21)$$

it follows that

$$\frac{1}{\alpha_1^2} - \frac{1}{\alpha_1} = \frac{c'_1}{K_1} \quad (22)$$

and

$$\frac{1}{\alpha_2^2} - \frac{1}{\alpha_2} = \frac{c'_2}{K_2} \quad (23)$$

On substituting in equation 22 the value of  $1/\alpha_1$  given in equation 18, we get

$$\left(1 + \frac{[\text{H}^+]}{K_1}\right)^2 - \left(1 + \frac{[\text{H}^+]}{K_1}\right) = \frac{c'_1}{K_1}$$

or, on solving for  $c'_1$  and simplifying,

$$c'_1 = [\text{H}^+] + \frac{[\text{H}^+]^2}{K_1} \quad (24)$$

With acids for which the value of  $K$  is small, the approximation

$$c'_1 = \frac{[\text{H}^+]^2}{K_1} \quad (25)$$

usually suffices. Similarly, it may be shown that

$$c'_2 = \frac{[\text{H}^+]^2}{K_2} \quad (26)$$

On combining equations 25 and 26, we obtain

$$\frac{c'_1}{c'_2} = \frac{K_2}{K_1} \quad (27)$$



Expressed in words: *two solutions of weak electrolytes are isohydric, and therefore may be mixed without the degree of dissociation of either undergoing any change, when the ratio of their concentrations before mixing is equal to the inverse ratio of their dissociation constants.*

In order to illustrate the application of this principle, let us calculate the concentrations and volumes of isohydric solutions of lactic acid ( $K = 1.4 \times 10^{-4}$ ) and trichloroacetic acid ( $K = 46.0 \times 10^{-4}$ ) that must be mixed, so as to give a liter of a solution containing 0.1 mole of lactic acid and 0.05 mole of trichloroacetic acid. It is evident from equation 27 that we should bring together solutions of lactic and trichloroacetic acids, the concentrations of which are in the ratio

$$c'_1 : c'_2 = K_2 : K_1 = 46.0 : 1.4 = 32.9 : 1$$

That is, the volume containing 0.05 mole of trichloroacetic acid must be 16.45 times as large as the volume containing 0.1 mole of lactic acid. These conditions will be satisfied if we mix 16.45/17.45 liter of a solution containing 0.05 mole of trichloroacetic acid with 1/17.45 liter of solution containing 0.1 mole of lactic acid. Hence, we must mix 942.7 cc of 0.053 normal trichloroacetic acid with 57.3 cc of 1.745 normal lactic acid.

**The Conductance of Mixed Acids.** When a mixture of two acids is formed by bringing together isohydric solutions of the acids, its specific conductance is readily calculated from the specific conductances of the isohydric solutions, and the volumes of each employed. If  $\kappa_1$  and  $\kappa_2$  represent the specific conductances of isohydric solutions of the acids  $\text{HA}_1$  and  $\text{HA}_2$ , respectively, then, on mixing  $v_1$  liters of the former with  $v_2$  liters of the latter, the specific conductance of  $\text{HA}_1$  will change to

$$\kappa'_1 = \frac{\kappa_1 v_1}{v_1 + v_2} \quad (28)$$

and that of  $\text{HA}_2$  to

$$\kappa'_2 = \frac{\kappa_2 v_2}{v_1 + v_2} \quad (29)$$

whence, the specific conductance of the mixture is

$$\begin{aligned} \kappa &= \kappa'_1 + \kappa'_2 \\ &= \frac{\kappa_1 v_1 + \kappa_2 v_2}{v_1 + v_2} \end{aligned} \quad (30)$$

The close agreement between the calculated and experimentally determined values of the specific conductances of mixtures formed

from isohydric solutions is shown by Hofmann's results<sup>1</sup> in Table CI.

TABLE CI  
SPECIFIC CONDUCTANCES OF MIXED ACIDS

Acids	Specific Conductance	
	Observed	Calculated
3.32 normal HBr	0.7504	.....
3.22 normal HCl	0.7441	.....
1 vol. HBr + 1 vol. HCl	0.7465	0.7472
1 vol. HBr + 3 vol. HCl	0.7470	0.7457
3 vol. HBr + 1 vol. HCl	0.7489	0.7488
4.99 normal H <sub>2</sub> SO <sub>4</sub>	0.7081	.....
3.22 normal HCl	0.7441	.....
1 vol. H <sub>2</sub> SO <sub>4</sub> + 1 vol. HCl	0.7244	0.7261
1 vol. H <sub>2</sub> SO <sub>4</sub> + 3 vol. HCl	0.7349	0.7351
3 vol. H <sub>2</sub> SO <sub>4</sub> + 1 vol. HCl	0.7169	0.7171

When the mixture of acids is formed from solutions which are not isohydric, the calculation of the conductance of the mixture from the conductances of its components is not so simple. Although the mixture can be regarded as being formed from isohydric solutions of its components, the determination of the unknown concentrations is often a matter of some difficulty. For a few simple cases, Wakeman<sup>2</sup> showed that these concentrations could be determined without much difficulty by the method of trial and error. This subject was also treated from the standpoint of isohydrism by Barmwater<sup>3</sup> and others.<sup>4</sup>

Although, when the component solutions are not isohydric, the conductance of a mixture of two electrolytes with a common ion is usually less than the mean of the component solutions taken singly,<sup>5</sup> the specific conductance of two such electrolytes in solvents of low dielectric constant is always higher than the calculated value. This has been ascribed

<sup>1</sup> *Z. physik. Chem.*, **45**, 584 (1903).

<sup>2</sup> *Z. physik. Chem.*, **15**, 159 (1894).

<sup>3</sup> *Ibid.*, **45**, 557 (1903).

<sup>4</sup> Cf. Kraus, *J. Am. Chem. Soc.*, **43**, 2507 (1921); Stearn, *ibid.*, **44**, 670 (1922). For other methods of calculating the conductance of mixtures, see Bray and Hunt, *ibid.*, **33**, 781 (1911); Schlesinger and Reed, *ibid.*, **41**, 1921 (1919); Kraus, *loc. cit.*

<sup>5</sup> Cf. Wolf, *Z. physik. Chem.*, **40**, 222 (1902).

to an increase in the dissociating power of the solvent, which is brought about by the second electrolyte.<sup>1</sup>

**The Water Correction in Conductance Measurements.** It has been pointed out in Chapter V that unless all conducting impurities are removed from the water, the measured conductance of an aqueous solution of an electrolyte is not that of the electrolyte alone; and that, when water is employed from which all conducting impurities except carbonic acid are excluded, it is necessary to make an exact correction for the conductance of this acid in order to obtain the conductance of the electrolyte in question. Although the "carbonic acid correction" is negligible for solutions of salts, and acids stronger than acetic acid, it becomes considerable for acids much weaker than this acid and for bases, even at ordinary concentrations. In the case of weak acids, the method of making the correction is as follows:<sup>2</sup>

Suppose that the conductance of a weak monobasic acid, HA, having a concentration  $c$ , has been measured at 25°. If  $x$  and  $y$  represent the concentrations of the A<sup>-</sup> ion and the HCO<sub>3</sub><sup>-</sup> ion, respectively, then we have the relation

$$\frac{(x+y)x}{(c-x)} = K_{\text{HA}}^{25^\circ} \quad (31)$$

and

$$\frac{(x+y)y}{(0.0000140 - y)} = K_{\text{H}_2\text{CO}_3}^{25^\circ} = 3.50 \times 10^{-7} \quad (32)$$

where 0.0000140 is the concentration in moles per liter of a saturated solution of carbonic acid under the partial pressure of the carbon dioxide of the atmosphere, and  $3.50 \times 10^{-7}$  is the dissociation constant of this acid, both at 25°. On solving these equations for  $x$  and  $y$ ,<sup>4</sup> we obtain the concentration of the HCO<sub>3</sub><sup>-</sup> ion, and from this we can calculate the fraction of the measured conductance due to carbonic acid. It would not be correct, however, to deduct this from the observed conductance and to call the result the conductance of the acid HA. Obviously, this difference would be the conductance of the acid in the presence, while what we desire is its conductance in the *absence*, of carbonic acid.

<sup>1</sup> Sachanov, *Z. physik. Chem.*, **89**, 441 (1914); Sachanov and Goncharov, *J. Russ. Phys. Chem. Soc.*, **47**, 1244 (1915).

<sup>2</sup> Kendall, *J. Am. Chem. Soc.*, **39**, 7 (1917); cf. Walker and Cormack, *J. Chem. Soc.*, **77**, 5 (1900).

<sup>3</sup> Kendall, *J. Am. Chem. Soc.*, **38**, 2465 (1916).

<sup>4</sup> This may be done by Horner's method or, more simply, by the method of trial and error.

If we represent by  $z$  the concentration of the  $A^-$  ions under these ideal conditions, then we may write

$$\frac{(x+y)x}{(c-x)} = \frac{z^2}{(c-z)} \quad (33)$$

For very weak acids, when the values of  $x$  and  $z$  are very small in comparison with that of  $c$ , the approximation

$$(x+y)x = z^2 \quad (34)$$

suffices. Here it is unnecessary to know the values of  $x$  and  $y$ , for, since

$$(x+y)x = (c-x)K_{HA} = z^2$$

we may use the approximation

$$z = \sqrt{K_{HA}c} \quad (35)$$

Since in the absence of carbonic acid the degree of dissociation of the acid at a concentration  $c$  is

$$\alpha = \frac{\Lambda_{corr.}}{\Lambda_0} = \frac{z}{c} \quad (36)$$

it follows that its corrected specific conductance is

$$k_{corr.} = \frac{c\Lambda_{corr.}}{10^3} = \frac{z\Lambda_0}{10^3} \quad (37)$$

TABLE CII

CORRECTION OF THE CONDUCTANCE OF SOLUTIONS OF PHENOL FOR THE PRESENCE OF CARBONIC ACID

Concentration Phenol in Moles per Liter	$x \cdot 10^6$	$y \cdot 10^6$	$z \cdot 10^6$	Specific Cond. $\times 10^6$		Equiv. Cond. Corrected	$K \times 10^{10}$	
				Uncorrected	Corrected		Uncorrected	Corrected
0.1240	3.39	0.2774	3.52	1.62	1.34	0.0108	1.47	1.00
0.0894	2.80	0.2868	2.99	1.43	1.14	0.0127	1.59	1.00
0.0620	2.35	0.2944	2.49	1.30	0.95	0.0153	1.87	1.01
0.0447	1.97	0.3012	2.11	1.15	0.80	0.0179	2.07	0.99
0.0310	1.61	0.3078	1.76	1.06	0.67	0.0216	2.53	1.00

The magnitude of the correction is illustrated for phenol in Table CII, where the corrections have been calculated with the use of the values  $\Delta_0\text{C}_6\text{H}_5\text{OH} = 380.0^1$  and  $K_{\text{C}_6\text{H}_5\text{OH}}^{25^\circ} = 10^{-7.2}$ .

**Double and Complex Salts.** In addition to electrolytes of simple composition, there are double salts and complex salts. By a double salt is meant a crystalline compound of several normal salts with one another, e.g., alum,  $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ . When a double salt is dissolved in water, it dissociates into the ions of the salts of which it is composed. On the other hand, complex salts, such as  $\text{K}_2\text{CdI}_4$  and  $\text{K}_4\text{Fe}(\text{CN})_6$ , dissociate the same way as ordinary salts. Thus, while a solution of kainite,  $\text{KCl} \cdot \text{MgSO}_4 \cdot 3\text{H}_2\text{O}$ , gives reactions for the potassium, magnesium, chlorine, and sulphate ions, a solution of potassium ferrocyanide does not give reactions for the ferrous ion or the cyanogen ion.

Although the conductance of a solution containing two salts is but *slightly* less than the calculated value, provided that reactions do not take place between the salts and their ions, when a complex salt is formed from the simple ions, the observed conductance is *much* less than the calculated value. Accordingly, the determination of the conductance of mixtures of salts has been extensively employed to determine the existence of complexes in solution; and a great deal of experimental data has been accumulated on this subject.<sup>3</sup> The two methods most largely used are: (1) the determination of the conductance of a mixture of simple salts in suitable concentrations and in molecular ratios corresponding to the composition of the supposed complex; and (2) the construction of conductance isotherms to ascertain whether the formation of complexes is disclosed by breaks in the curves. A sharp break in the curve appears to be possible only when a perfect complex, which is practically undissociated, is formed.<sup>4</sup> Otherwise, the break is more and more rounded, the more extensively the complex is dissociated. This convexity is not characteristic of complexes, since it is exhibited by mixtures in which complex formation is known to be absent.

Solutions of double salts often exhibit a conductance which is very appreciably less than the calculated value. It was shown by Jones and Mackay<sup>5</sup> that, though the difference between the two values becomes

<sup>1</sup> Kendall, *J. Am. Chem. Soc.*, **39**, 7 (1917).

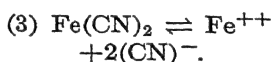
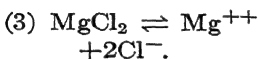
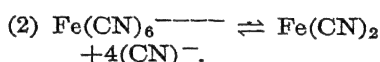
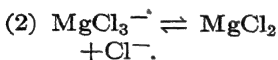
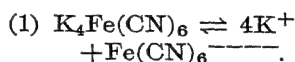
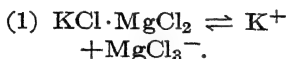
<sup>2</sup> Cf. Lundén, *Z. physik. Chem.*, **70**, 251 (1910); and Boyd, *J. Chem. Soc.*, **107**, 1540 (1915). A small error in this value will not affect the correction appreciably.

<sup>3</sup> Cf. Morgan, *Z. physik. Chem.*, **17**, 513 (1895); Jones and Bassett, *Am. Chem. J.*, **34**, 313 (1905); Sandonnini, *Atti ist. Veneto sci.*, **74**, 519 (1915) (this paper contains a bibliography); Burrows and Turner, *J. Chem. Soc.*, **115**, 1429 (1919); Burrows, *ibid.*, **123**, 2026 (1923).

<sup>4</sup> Sandonnini, *loc. cit.*

<sup>5</sup> *Am. Chem. J.*, **19**, 83 (1897); cf. also Bender, *Wied. Ann.*, **22**, 179 (1884); Klein, *ibid.*, **27**, 151 (1886); Archibald, *Trans. Nova Scotian Inst. Sci.*, **9**, 307 (1891).

less as the concentration of the solution decreases, the calculated and the observed conductances agree only for very dilute solutions. It is probable, therefore, that except at very low concentrations complex ions exist in solutions of double salts. Since Morgan <sup>1</sup> showed that a normal solution of potassium ferrocyanide contains 0.000533 equivalent per liter of the simple cyanogen ion, it is likely that the process of dissociation is the same for double and complex salts, and that the distinction made above is one of degree rather than of kind. The dissociation of a double salt, such as carnallite, and a complex salt, like potassium ferrocyanide, may be represented as follows:



For double salts, the dissociation corresponding to (2) is almost complete; for complex salts this dissociation takes place to but a very limited extent.

TABLE CIII  
DISSOCIATION OF COBALT COMPLEXES

Type	Example	Formula	Ions
[CoA <sub>6</sub> ]R <sub>3</sub>	Hexammine-cobaltic chloride	[Co(NH <sub>3</sub> ) <sub>6</sub> ]Cl <sub>3</sub>	[Co(NH <sub>3</sub> ) <sub>6</sub> ] <sup>+++</sup> 3Cl <sup>-</sup>
[CoA <sub>5</sub> R]R <sub>2</sub>	Nitritopentammine-cobaltic chloride	[Co(NH <sub>3</sub> ) <sub>5</sub> NO <sub>2</sub> ]Cl <sub>2</sub>	[Co(NH <sub>3</sub> ) <sub>5</sub> NO <sub>2</sub> ] <sup>++</sup> 2Cl <sup>-</sup>
[CoA <sub>4</sub> R <sub>2</sub> ]R	Dichlorotetrammine-cobaltic nitrate	[Co(NH <sub>3</sub> ) <sub>4</sub> Cl <sub>2</sub> ]NO <sub>3</sub>	[Co(NH <sub>3</sub> ) <sub>4</sub> Cl <sub>2</sub> ] <sup>+</sup> NO <sub>3</sub> <sup>-</sup>
[CoA <sub>3</sub> R <sub>3</sub> ]	Trinitritotriammine cobalt	[Co(NH <sub>3</sub> ) <sub>3</sub> (NO <sub>2</sub> ) <sub>3</sub> ]	no ions
[CoA <sub>2</sub> R <sub>4</sub> ]M	Potassium tetranitritodiammincobaltate	[Co(NH <sub>3</sub> ) <sub>2</sub> (NO <sub>2</sub> ) <sub>4</sub> ]K	K <sup>+</sup> [Co(NH <sub>3</sub> ) <sub>2</sub> (NO <sub>2</sub> ) <sub>4</sub> ] <sup>-</sup>
[CoAR <sub>5</sub> ]M <sub>2</sub>	Potassium pentanitritodiammincobaltate	[Co(NH <sub>3</sub> )(NO <sub>2</sub> ) <sub>5</sub> ]K <sub>2</sub>	2K <sup>+</sup> [Co(NH <sub>3</sub> )(NO <sub>2</sub> ) <sub>5</sub> ] <sup>---</sup>
[CoR <sub>6</sub> ]M <sub>3</sub>	Potassium hexanitritocobaltate	[Co(NO <sub>2</sub> ) <sub>6</sub> ]K <sub>3</sub>	3K <sup>+</sup> [Co(NO <sub>2</sub> ) <sub>6</sub> ] <sup>---</sup>

<sup>1</sup> *Z. physik. Chem.*, 17, 513 (1895).

**The Dissociation of the Metal Ammines.** The compounds formed by platinum, iridium, cobalt, and chromium with ammonia—the metal ammines—constitute a type of complex that deserves mention. Each of these metals forms several series of complexes with ammonia. The number and nature of the ions into which they dissociate depend upon the number of ammonia molecules contained in the complex. This is illustrated by Table CIII for a number of cobalt complexes.

This table shows the gradual transition from a trivalent cation,  $[\text{Co}(\text{NH}_3)_6]^{+++}$ , to a trivalent anion,  $[\text{Co}(\text{NO}_2)_6]^{---}$ , through the intermediate formation of a non-electrolyte,  $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$ .

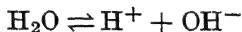
### PROBLEMS

1. One liter of a solution contains 2 moles of acetic acid and 0.5 mole of cyanacetic acid. Given that the degrees of dissociation of the acids in the mixture are 0.000421 and 0.0835 per cent, respectively, calculate the dissociation constant of each acid.
2. What is the concentration of a solution of acetic acid ( $K = 1.8 \times 10^{-5}$ ) that is isohydric with a 0.01 normal solution of cyanacetic acid ( $K = 370 \times 10^{-5}$ )?
3. Calculate the volumes and concentrations of isohydric solutions of monochloroacetic acid ( $K = 155 \times 10^{-5}$ ) and dichloroacetic acid ( $K = 5140 \times 10^{-5}$ ) that must be mixed, so as to give 1 liter of a solution containing 0.1 mole of each acid.
4. Calculate the volumes and concentrations of isohydric solutions of benzoic acid ( $K = 6.6 \times 10^{-5}$ ) and salicylic acid ( $K = 105 \times 10^{-5}$ ) that must be mixed, so as to give 1 liter of a solution containing 0.2 mole of benzoic acid and 0.05 mole of salicylic acid.
5. If to a liter of 0.02 normal benzoic acid 2 grams of *ortho*-nitrobenzoic acid ( $K = 615 \times 10^{-5}$ ) is added, what will be the percentage dissociation of each acid in the mixture?
6. How many grams of bromoacetic acid ( $K = 138 \times 10^{-5}$ ) must be added to a liter of normal acetic acid ( $K = 1.8 \times 10^{-5}$ ), so as to reduce the degree of dissociation of the acetic acid to one-half?
7. At zero concentration, the equivalent conductance of acetic acid ( $K = 1.8 \times 10^{-5}$ ) is 348 at 18°. Calculate the equivalent conductance of this acid in a mixture containing 0.5 mole of acetic acid and 0.1 mole of monochloroacetic acid ( $K = 155 \times 10^{-5}$ ) per liter.
8. At 54°, the velocity constant of the inversion of cane sugar by 0.0125 normal hydrochloric acid is 0.00469, and that of the inversion by 0.25 normal acetic acid is 0.00075. Assuming that the velocity constant is directly proportional to the concentration of the hydrogen ion, and, at the above concentration, that hydrochloric acid is completely dissociated, calculate (a) the hydrogen-ion concentration, (b) the degree of dissociation, and (c) the dissociation constant of the acetic acid.
9. (Cf. preceding problem.) Calculate the velocity constant of the inversion of cane sugar at 54° by a mixture of 0.25 normal acetic acid and 0.125 normal sodium acetate which is completely dissociated.
10. The dissociation constant of ammonium hydroxide is  $2.3 \times 10^{-5}$  at 25°. Calculate the percentage dissociation of ammonium hydroxide in a solution containing 0.1 equivalent each of the base and ammonium chloride per liter, assuming that the degree of dissociation of the salt in the mixture is 100 per cent.

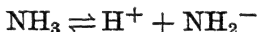
## CHAPTER XVIII

### THE DISSOCIATION OF WATER

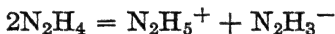
Thus far in our discussion of ionic equilibria in aqueous solutions, the influence of the possible dissociation of the solvent has been left entirely out of consideration. It has long been known, however, that very pure water possesses a small conductance, due to the dissociation



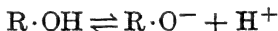
Likewise in ammonia we have the reaction



and in hydrazine the reaction <sup>1</sup>



Some other solvents have also been found to be dissociated more or less. For example, three lines of evidence <sup>2</sup> indicate that alcohols are weak acids, dissociation taking place in accordance with the equation



For ethyl alcohol, this dissociation amounts to about 8 per cent that of water.

**The Ionic Product of Water.** The dissociation of water is expressed by the equation

$$K = \frac{[\text{H}^+][\text{OH}^-]}{[\text{HOH}]}$$

or, since the concentration of the undissociated water molecules may be regarded as constant,

$$K_w = [\text{H}^+][\text{OH}^-] \quad (1)$$

The constant  $K_w$ , called the **ionic product of water**, has a value of about  $10^{-14}$  at  $25^\circ$ . This means that in pure water, each ion has a concentration of about  $10^{-7}$  equivalent per liter, or in other words, water is one

<sup>1</sup> Pleskov, *Acta Physicochim. U.R.S.S.*, **13**, 662 (1940).

<sup>2</sup> Williams and Trusdail, *J. Am. Chem. Soc.*, **45**, 1348 (1923); cf. Danner and Hildebrand, *ibid.*, **44**, 2824, 2832 (1922).



ten-millionth normal with respect to each of its ions. Determinations of the value of the ionic product of water have been carried out by several completely independent methods, and in every determination substantially the same value has been obtained.

**The Conductance Method.** Ordinary distilled water has a specific conductance of  $3 - 6 \times 10^{-6}$  mho, or even higher, which is largely due to the presence of such substances as ammonium salts, carbonic acid, glass, etc., dissolved from the atmosphere and from the containing vessel. By exercising the most scrupulous care, Kohlrausch and Heydweiller<sup>1</sup> prepared water of a very high degree of purity. The water was finally distilled in platinum vessels *in vacuo*, as contact with the atmosphere rapidly increased the impurities. The specific conductance of their purest water was then measured, and the following results obtained at different temperatures:

Temperatures:	0°	18°	25°	34°	50
Specific conductance $\times 10^6$ :	0.014	0.040	0.058	0.089	0.176

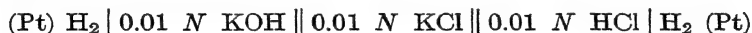
From the value of the specific conductance at 18°, and the values of the conductances of the hydrogen and hydroxyl ions at this temperature, the concentration of each of the ions of water can be readily calculated. One equivalent each of hydrogen and hydroxyl ions, when placed between electrodes which are 1 centimeter apart, would have a conductance of  $\Lambda_{H^+} + \Lambda_{OH^-} = 313 + 174$ , at 18°. If, now, these quantities of the ions could be placed between electrodes which were 1 square centimeter in cross section and 1 centimeter apart, the conductance, which would remain unchanged, would represent the specific conductance. It is evident, therefore, that since a specific conductance of 487 mhos corresponds to one equivalent of each kind of ion in 1 cc, a specific conductance of  $0.040 \times 10^{-6}$  mho must correspond to  $\frac{0.040 \times 10^{-6}}{487} \times 1000 = 0.82 \times 10^{-7}$  equivalent of each kind of ion per liter. The square of this value is the ionic product of water.

**The Saponification Method.** It has been mentioned on p. 44 that certain reactions are catalyzed by the hydroxyl ion. For example, the saponification of certain esters, such as ethyl acetate, is accelerated by the presence of hydroxyl ions. Since the velocity constants of such reactions are directly proportional to the concentration of the hydroxyl ions present, this phenomenon may be employed to determine the concentration of hydroxyl ions present in a solution. This is done by first determining the velocity constant when the reaction is catalyzed by a

<sup>1</sup> *Wied. Ann.*, 53, 209 (1894); *Z. physik. Chem.*, 14, 317 (1894).

known concentration of hydroxyl ions (a dilute solution of sodium or potassium hydroxide), and then when the reaction is catalyzed by the solution of unknown hydroxyl-ion concentration. This method was employed by Wijs<sup>1</sup> to determine the concentration of the hydroxyl ions in water. Wijs allowed methyl acetate and water to react at 25°. This reaction is accelerated by both the hydrogen and hydroxyl ions of the water, but as the reaction conditioned by the hydroxyl ions proceeds much more rapidly than that affected by the hydrogen ions, the reaction may be supposed to be caused solely by the former ions. Wijs followed the progress of the reaction by titrating the liberated acetic acid, from time to time, with standard alkali. Only the first few titrations were considered, since the free acetic acid contributes a large number of hydrogen ions as the reaction proceeds. From the rate of decomposition, a value for the time  $t = 0$  was obtained by extrapolation, and from this value the concentration of the hydroxyl ions in water was calculated to be  $1.4 \times 10^{-7}$ , at 25°.

**The Electromotive-Force Method.** It has been shown (p. 216) that the hydrogen-ion concentration of a solution may be determined by electromotive-force measurements. At 25°, the electromotive force of the cell.



is given by the expression

$$E = 0.059 \left( \log \frac{C_1}{C_2} - \log \frac{u_{\text{H}} + v_{\text{Cl}}}{u_{\text{K}} + v_{\text{Cl}}} - \log \frac{u_{\text{K}} + v_{\text{OH}}}{u_{\text{K}} + v_{\text{Cl}}} \right) \quad (2)$$

where  $C_1$  and  $C_2$  are the concentrations of hydrogen ions in the acid and alkali solutions, respectively. Since all the other quantities in this equation are known, or can be measured, the concentration,  $C_2$ , of the hydrogen ions in the alkali solution can be calculated. If  $C$  represents the concentration of the hydroxyl ions in the alkali solution, then we have

$$C \times C_2 = K_w \quad (3)$$

This method, which requires less precision than those preceding, was first employed by Ostwald,<sup>2</sup> with results substantially the same as those obtained by other methods.

By means of electromotive-force measurements, Harned and Hamer<sup>3</sup>

<sup>1</sup> *Z. physik. Chem.*, **11**, 492 (1893).

<sup>2</sup> *Ibid.*, **11**, 521 (1893).

<sup>3</sup> *J. Am. Chem. Soc.*, **55**, 2194 (1933); see also Harned and Robinson, *Trans. Faraday Soc.*, **36**, 973 (1940).

determined the ionic product of water between 0° and 60°. Their results are expressed by the equation

$$\log K_w = -\frac{4787.3}{T} - 7.1321 \cdot \log T - 0.010365T + 22.801$$

The value given by this equation for 25° is in close agreement with that obtained by Lewis, Brighton, and Sebastian<sup>1</sup> for the same temperature.

From electromotive-force data, Harned<sup>2</sup> calculated the value of the

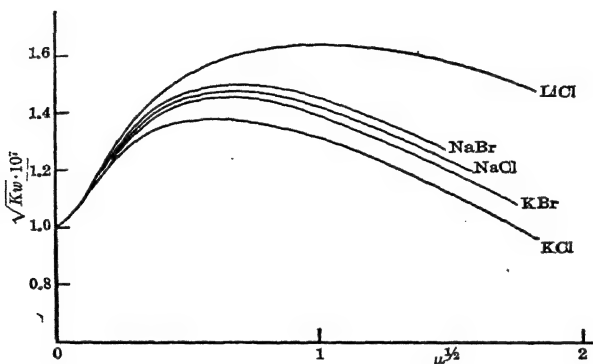


FIG. 85.

ionic product of water in several salt solutions. His results are shown graphically in Fig. 85, where the square root of the ionic product is plotted against the square root of the ionic strength of the solution.

**The Hydrolytic Method.** The study of the hydrolysis of salts (see following chapter) also affords an important means of determining the ionic product of water. By this method, Shields<sup>3</sup> obtained data which gave the value  $1.27 \times 10^{-14}$  for the ionic product of water at 25°. Later, this method was also employed by Noyes and his co-workers<sup>4</sup> and by Lundén<sup>5</sup> to determine the variation of the value of the ionic product of water with change in temperature. In Table CIV are given some of the values obtained, together with those calculated from Kohlrausch and Heydweiller's conductance data.

<sup>1</sup> *J. Am. Chem. Soc.*, **39**, 2245 (1917).

<sup>2</sup> *Ibid.*, **47**, 930 (1925); *Trans. Am. Electrochem. Soc.*, **51**, 571 (1927).

<sup>3</sup> *Z. physik. Chem.*, **12**, 167 (1893).

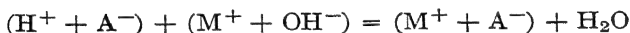
<sup>4</sup> *J. Am. Chem. Soc.*, **29**, 1402 (1907); **32**, 159 (1910).

<sup>5</sup> *Z. physik. Chem.*, **70**, 249 (1910).

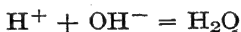
TABLE CIV  
VALUES OF THE IONIC PRODUCT OF WATER

Temperature	$K_w \times 10^{14}$		
	K. and H.	Lundén	Noyes
0°	0.12	....	0.089
10°	0.31	0.29	....
18°	0.64	....	0.46
25°	1.11	0.99	0.82
40°	3.26	2.86	....
50°	6.15	5.31	....
100°	....	....	48
156°	....	....	223
218°	....	....	461
306°	....	....	168

**Neutralization.** The extremely small value of the ionic product of water simply means that the hydrogen and hydroxyl ions unite so completely that only very small, but definite, concentrations of these ions can exist in the same solution. If, therefore, high concentrations of these ions are brought together in the same solution, as when a solution of an acid is added to a solution of a base, it is obvious that equilibrium cannot exist, and that the hydrogen and hydroxyl ions must unite until their concentrations are reduced to such an extent that their product does not exceed  $10^{-14}$ . When the salt formed by the neutralization of an acid and a base is completely dissociated, as often happens, the process of neutralization may be expressed thus



or simply



That is, the process of the neutralization of a strong acid by a strong base consists merely in the formation of undissociated molecules of water from hydrogen and hydroxyl ions.

**Heat of Neutralization and Dissociation.** Many years ago (1840), the Russian thermochemist, Hess,<sup>1</sup> made the remarkable discovery (one

<sup>1</sup> Ostwald's *Klassiker exakt. Wiss.*, No. 9.

which was inexplicable at the time) that, when a gram equivalent of a strong acid was neutralized with a gram equivalent of a strong base, 13,700 calories of heat were developed. This quantity of heat is called the heat of neutralization. In the light of what has just been said, it is evident that the same quantities of heat should be evolved during the neutralization of equivalent quantities of strong acids and bases. Later

TABLE CV  
HEATS OF NEUTRALIZATION

Acid	Amount of Water Associated with One Mole of Acid	Heat of Neutral- ization *
<i>Monobasic Acids</i>	Moles	Calories
Hydrobromic	200	-13,750
Hydrochloric	200	-13,780
Hydriodic	200	-13,680
Chloric	400	-13,760
Bromic	400	-13,780
Nitric	200	-13,680
Formic	200	-13,450
Acetic	200	-13,400
Propionic	200	-13,480
Trichloroacetic	200	-13,920
<i>Polybasic Acids</i>		
Hydrofluosilicic	200	-13,310
Hydrogen platonic chloride	600	-13,610
Selenious	200	-13,510
Dithionic	600	-13,535
Oxalic	300	-14,140
Malic	200	-13,085
Aconitic	200	-13,037

\* Following the custom of thermodynamics, heat developed is taken as negative.

investigation showed that in many cases of neutralization the quantity of heat developed was not 13,700 calories, but sometimes more and sometimes less than this quantity. The painstaking investigations of the Swedish thermochemist, Thomsen, who determined the heat of neutralization of 31 inorganic and 14 organic acids, were productive of numerous thermochemical data. In Table CV are given the quantities of heat Thomsen found to be produced <sup>1</sup> when a gram equivalent of each of a

<sup>1</sup> *Thermochemische Untersuchungen*, I, pp. 149-309, 1882; cf. *Thermochemistry*, translated by Burke, 1908.

number of acids was neutralized by an equivalent quantity of 0.005 normal sodium hydroxide solution.

In the neutralization of partially dissociated acids or bases, or when the salts formed are not completely dissociated, the process cannot be represented simply by the equation



for the ionization of the undissociated molecules of acid or base and the formation of undissociated molecules of salt must be taken into consideration. In accordance with the law of mass action, the equilibrium between the hydrogen and hydroxyl ions of the undissociated molecules of acid and base is disturbed when these ions unite to form water, and, in consequence, further dissociation of the undissociated molecules takes place. Since the dissociation of a molecule into its ions is usually attended by a heat change, it is evident that the heat of neutralization will be greater or less than 13,700 calories, according as the dissociation of the acid or the base is an exothermic or an endothermic process. In Table CVI are given the heat of neutralization and the heat of dis-

TABLE CVI  
HEATS OF NEUTRALIZATION AND DISSOCIATION

Acid	Heat of Dissociation at 21.5°, calories	Heat of Neutralization at 18–20°, calories
Succinic	+1,115	–12,080
Dichloroacetic	–2,924	–14,830
Hypophosphorus	–3,745	–15,160

sociation (i.e., the heat absorbed where one mole of an electrolyte dissociates into its ions) of a few acids. Following the custom of thermodynamics, exothermic dissociation is taken as negative and endothermic dissociation as positive.

Results similar to those discussed for acids have been obtained for bases.

Thomsen showed that, when an aqueous solution of an acid is added to a solution containing one gram equivalent of a base, the quantity of heat developed is very nearly proportional to the amount of acid added, until the acid reaches one gram-equivalent, after which very little thermal effect is observed. When dilute solutions of salts are mixed, no heat change is observed. This thermoneutrality indicates that the ions undergo little or no change on mixing two dilute salt solutions (which do not form an insoluble compound).

**The Heat of Dissociation of Water.** Since 13,700 calories of heat are evolved when one gram ion each of hydrogen and hydroxyl unite to form undissociated water, it may be inferred that this same quantity of heat must be absorbed whenever one mole of water dissociates into its ions. The heat of dissociation of water is, therefore, +13,700 calories. By studying the variation of the dissociation of water with temperature, it has been possible to test the validity of this inference.

Equation 21, Chapter VIII, may be written in the form

$$A = RT \ln K - RT \sum m \ln B \quad (4)$$

The variation of  $A$  with temperature (at constant volume) may be obtained by differentiating this equation with respect to  $T$ , thus:

$$\left(\frac{dA}{dT}\right)_v = R \ln K + RT \frac{d(\ln K)}{dT} - R \sum m \ln B - RT \frac{d(\sum m \ln B)}{dT} \quad (5)$$

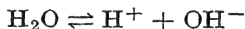
Since the arbitrarily chosen concentrations denoted by  $\Sigma B^m$  are independent of changes in temperature, the last term of the second member of equation 5 is equal to zero, and we have:

$$\left(\frac{dA}{dT}\right)_v = R \ln K + RT \frac{d(\ln K)}{dT} - R \sum m \ln B \quad (6)$$

On substituting these values of  $A$  and  $(dA/dT)_v$  in equation 11, Chapter VIII, and remembering that  $U = -q_v$  (equation 10, Chapter VIII), where  $-q_v$  is the heat evolved by the reaction at constant volume, we obtain the equation of the *reaction isochore*

$$\frac{d \ln K}{dT} = \frac{q_v}{RT^2} \quad (7)$$

Here  $q$  is the heat absorbed by the reaction. For the equilibrium



equation 7 may be written

$$\frac{d \ln K_w}{dT} = \frac{q}{RT^2} \quad (8)$$

where  $q$  is the heat of dissociation of water. Although this equation ceases to be even approximate at high temperatures, when the vapor pressure of water is high, it gives good results at lower temperatures.

If it is assumed that the heat of dissociation,  $q$ , is a linear function of the temperature, i.e., that

$$q = q_0 + aRT \quad (9)$$

(where  $a$  is a constant), on integrating equation 8 we obtain:

$$\ln \cdot \frac{K'_w}{K''_w} - a \cdot \ln \cdot \frac{T'}{T''} = \frac{q_0}{R} \frac{T' - T''}{T'T''} \quad (10)$$

From the data (Noyes') given in Table CIV for the ionic product of water at 0°, 25°, and 100°, the values 28,460 and -24.923 have been obtained for the constants  $q_0$  and  $a$ , respectively. On substituting these values in equation 9, we obtain the expression

$$q = 28,460 - 49.5T \quad (11)$$

for the heat of dissociation of water at a temperature  $T$ .

By means of equations 10 and 11, Noyes calculated the heat of dissociation and the ionic product of water at a number of temperatures. His results are given in Table CVII. The values calculated for the heat

TABLE CVII

HEAT OF DISSOCIATION AND THE IONIC PRODUCT OF WATER

Temperatures	Heat of Dissociation $q$ , calories	Ionic Product $K_w \times 10^{14}$
0°	14,950	0.088
18°	14,055	0.46
25°	13,710	0.81
50°	12,470	4.5
75°	11,230	16.9
100°	9,995	48
128°	8,610	114
156°	7,225	217
218°	(4,155)	(512)

of dissociation of water at 0° and 25° agree closely with those determined experimentally by Wörman,<sup>1</sup> who obtained the mean values 14,710 calories at 0° and 13,410 calories at 25°, from measurements of the heat of neutralization of nitric and hydrochloric acids by sodium and potassium hydroxides.

Although the values obtained by Noyes for the ionic product of water at 0°, 25°, and 100° must necessarily agree with those determined by experiment (see Table CIV), the close agreement between the calculated

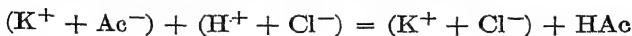
<sup>1</sup> *Ann. Physik*, (4), 18, 793 (1905).



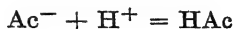
and experimental values at 18° and 156° is remarkable. The values in Table CVII show that, up to 156°, equation 8 is correct, and, therefore, that values calculated for the ionic product of water between 0° and this temperature are substantially correct. Even at 218° the difference between the experimental and the calculated values is not large. The data given in Table CVII indicate that the heat of dissociation of water decreases more rapidly at temperatures above 156° than at ones below it. In accordance with equation 11, the heat of dissociation of water should become zero, and, therefore, the ionic product should attain its maximum value at 302°. From the experimental data in Table CIV, it is evident that the ionic product of water reaches its maximum value at a temperature between 250° and 275°, and that above this temperature the value for the heat of dissociation becomes negative. Above this temperature, therefore, the neutralization of dissociated acids and bases would be an endothermic process.

**The Influence of Temperature on the Dissociation of Water.** The increase in the value of the ionic product of water with rise in temperature must be due to an increase in the concentration of the hydrogen and hydroxyl ions. Unlike most other electrolytes (see Table XXV) the dissociation of water continues to increase with temperature up to 250° or 275°. This phenomenon, Noyes points out, is probably due to the fact that whereas at lower temperatures water consists mostly of complex molecules, containing only a small proportion of simple water molecules, the proportion of the simple molecules increases rapidly with rise in temperature. This assumption was shown to be correct by Guye<sup>1</sup> and others.<sup>2</sup> In accordance with the law of mass action, an increase in the concentration of the simple water molecules must bring about an increase in the concentration of the hydrogen and hydroxyl ions. Therefore, even though, like most other electrolytes, the degree of dissociation of water decreases with rise in temperature, the concentration of its ions will steadily increase with rising temperature, until a certain fraction of the polymerized water molecules has decomposed.

**The Heat of Dissociation of Weak Acids and Bases.** The heat of dissociation of weak acids and bases may be calculated by means of equation 8, or it may be determined calorimetrically. Since when a salt of a weak acid is decomposed by a strong acid, e.g.,



or simply



<sup>1</sup> *Trans. Faraday Soc.*, **6**, 71 (1911).

<sup>2</sup> Cf. Richards and Palitsch; *J. Am. Chem. Soc.*, **41**, 59 (1919).

practically all the salt is converted into the undissociated acid, it is obvious that the heat of reaction is identical with the heat of dissociation of the acid. In Table CVIII are given values of the heats of dissociation

TABLE CVIII  
HEATS OF DISSOCIATION OF WEAK ACIDS

Acid	Temperature, °C	Heat of Dissociation, calories
<i>o</i> -Aminobenzoic acid	20	+3,465
Benzoic acid	20	+370
Fumaric acid	12.5	+970
Maleic acid	12.5	+850
Masaconic acid	12.5	+520
Malonic acid	12.5	+970
<i>m</i> -Phthalic acid	12.5	+2,260
Monochloroacetic acid	12.5	-1,000
Nitrourea	20	+4,000
Nitrourethane	20	+3,200
<i>o</i> -Chlorobenzoic acid	20	-2,060
Violuric acid	25	+3,700
Saccharose	25	+10,150
<i>d</i> -Glucose	25	+8,110
<i>d</i> -Fructose	25	+6,580
Hydrocyanic acid	25	+10,050

of a number of weak acids. These values, which were obtained by Lundén,<sup>1</sup> Euler,<sup>2</sup> Kortright,<sup>3</sup> Baur,<sup>4</sup> Schaller,<sup>5</sup> Abegg,<sup>6</sup> and Madsen,<sup>7</sup> show that the heat of dissociation of very weak acids (the last four in the table) is large and positive (endothermic). The same is true for very weak bases. No such rule appears to hold for moderately weak acids and bases. The heat of dissociation of such electrolytes may be large or small, positive or negative.

### PROBLEMS

1. Given that the value of the gas constant is 1.99 (thermal units), calculate the heat of dissociation of water at 0°, 20°, 40°, 60°, 80°, and 100°. Plot the values obtained against the corresponding temperatures, and join the points by a smooth curve.

<sup>1</sup> *Z. physik. Chem.*, **54**, 532 (1906).

<sup>2</sup> *Ibid.*, **21**, 257 (1896).

<sup>3</sup> *Am. Chem. J.*, **18**, 365 (1896).

<sup>4</sup> *Z. physik. Chem.*, **23**, 409 (1897); *Ann.*, **296**, 95 (1897).

<sup>5</sup> *Z. physik. Chem.*, **25**, 497 (1898).

<sup>6</sup> *Ber.*, **33**, 393, 626 (1900).

<sup>7</sup> *Z. physik. Chem.*, **36**, 290 (1901).

2. Given that the specific conductance of water is  $0.176 \times 10^{-6}$  mho at  $50^\circ$ , calculate its ionic product at this temperature. With the value obtained, calculate the ionic product of water at  $70^\circ$ .

3. On mixing 100 cc of a 0.5 normal solution of potassium hydroxide (temperature =  $18.76^\circ$ ) with an equal volume of 0.5 normal hydrochloric acid (temperature =  $18.98^\circ$ ), the temperature of the mixture rose to  $22.30^\circ$ . Assuming that the specific heat of the mixture is equal to unity, calculate the heat of dissociation of water.

4. On mixing 100 cc of a 0.2 normal solution of sodium dichloroacetate with an equal volume of hydrochloric acid of the same strength (both solutions at  $20.00^\circ$ ), the temperature of the mixture rose to  $20.207^\circ$ . Assuming that the specific heat of the mixture is unity, and that equilibrium is established when 75 per cent of the salt has decomposed, calculate the heat of dissociation of dichloroacetic acid.

5. Calculate the electromotive force of the cell.



at  $18^\circ$ , being given that the ionic product of water is  $10^{-14}$ , and assuming that the electrolytes are completely dissociated.

## CHAPTER XIX

### HYDROLYSIS

In Chapter XVII it was pointed out that when high concentrations of the anions of a weak acid and hydrogen ions, or the cations of a weak base and hydroxyl ions, are brought together in the same solution, these ions unite to form undissociated molecules of the weak acid or weak base. Moreover, it was shown that this union continues until the value of the ratio of the product of the concentrations of the ions of the acid, or base, to the concentration of its undissociated molecules is reduced to the value of the dissociation constant of the weak acid, or base. In the preceding chapter we have seen that water has a small but measurable concentration of hydrogen and hydroxyl ions. We have now to discuss to what extent the concentrations of the ions of water influence the equilibria between the ions and undissociated molecules of electrolytes.

**Hydrolysis.** From what has been said previously, it is obvious that, if we dissolve a salt of an acid in water, some of the undissociated acid must form, and that its amount will be greater, the smaller the dissociation constant of the acid. When, for example, sodium chloride is dissolved in water, the amount of undissociated hydrochloric acid formed is infinitesimal.

The influence of the hydrogen or hydroxyl ions of water is quite different in a solution of a dissociated salt of a weak acid (HA) or a weak base (MOH). Here it is evident that the value of the ratio

$$\frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \quad \text{or} \quad \frac{[\text{M}^+][\text{OH}^-]}{[\text{MOH}]}$$

must at first exceed the value of the small dissociation constant of the acid or base. Therefore, in order that this value be established, undissociated acid, or undissociated base, must form at the expense of the ions, and the amount formed must be greater, the smaller the dissociation constant of the acid, or base. To the phenomenon of the union of the ions of water with the ions of a salt the name **hydrolysis** has been given.

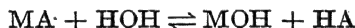
**The Degree of Hydrolysis and the Hydrolytic Constant.** In order to determine the extent to which hydrolysis occurs in solution, let us consider a solution of a uniunivalent salt (MA) of a strong base and a weak

acid, containing  $c$  moles per liter. Since the hydroxide (MOH) is highly (or completely) dissociated, there is little or no reaction between the  $M^+$  ions of the salt and the hydroxyl ions of the water. On the other hand, the  $A^-$  ions of the salt and the hydrogen ions of the water react, to a greater or less extent, to form the undissociated acid, HA. In an aqueous solution of the salt there exist the equilibria expressed by the following equations:

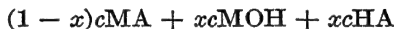
$$\frac{[H^+][A^-]}{[HA]} = K_a \text{ (small)} \quad (1)$$

$$[H^+][OH^-] = K_w = 1.2 \times 10^{-14} \quad (2)$$

Let us represent the degree of hydrolysis or the fraction of each mole of salt that hydrolyzes by  $x$ . After the hydrolysis



has taken place and equilibrium has been established there will be in the solution



Since in the presence of the dissociated salt, MA, the dissociation of the weak acid is negligible, the concentration of the undissociated molecules of this acid may be taken as  $xc$ . Further, if  $\alpha_1$  represents the degree of dissociation of the salt, then the concentration of the  $A^-$  ions may be taken as  $(1-x)\alpha_1$ . If  $\alpha_2$  represents the degree of dissociation of the base, the concentration of the hydroxyl ions is  $x\alpha_2$ ; and because

$$[H^+][OH^-] = K_w$$

it follows that

$$[H^+] = \frac{K_w}{x\alpha_2} \quad (3)$$

On substituting these values in equation 1, we obtain:

$$K_a = \frac{\frac{K_w}{x\alpha_2} (1-x)\alpha_1}{xc} = K_w \frac{(1-x)\alpha_1}{x^2\alpha_2} \quad (4)$$

When the salt MA and the strong base MOH are both highly (or completely) dissociated, as they usually are, it may be assumed that  $\alpha_1 = \alpha_2$ . Therefore equation 4 may be written

$$\frac{K_w}{K_a} = \frac{x^2c}{(1-x)} = \text{the hydrolytic constant} \quad (5)$$

This expression is analogous in form to the dilution law. Just as the

	(Concn. cations)	(Concn. anions)	
Dissociation constant	(Concn. undissociated salt)		
so the			
	(Concn. acid)	(Concn. base)	
Hydrolytic constant	(Concn. unhydrolyzed salt)		(6)

On solving equation 5 for  $x$ , we obtain:

$$x = \frac{-1}{2c} \cdot \frac{K_w}{K_a} + \sqrt{\frac{1}{4c^2} \cdot \left(\frac{K_w}{K_a}\right)^2 + \frac{1}{c} \cdot \frac{K_w}{K_a}} \quad (7)$$

When the dissociation constant of the weak acid is very much greater than the ionic product of water, i.e., when the ratio  $K_w:K_a$  is small, equation 7 reduces to

$$x = \sqrt{\frac{1}{c} \frac{K_w}{K_a}} \quad (8)$$

It will be observed that if the total concentration  $c$  of the salt, the ionic product of water, and the dissociation constant  $K_a$  of the acid are known, the degree of hydrolysis,  $x$ , of any salt of a strong base and a weak acid may be calculated by means of equation 7 or 8. Conversely, from the degree of hydrolysis and the concentration of the salt, the ionic product of water or the dissociation constant of the weak acid may be calculated, provided that the other is known. Hydrolysis measurements afford an important means of determining the dissociation constants of weak acids and bases.

Since the concentration  $c$  and the dissociation constant  $K_a$  are contained in the denominator of equations 7 and 8, it is evident that the degree of hydrolysis of a salt of a strong base and a weak acid must be greater, the smaller the concentration of the salt and the smaller the dissociation constant of the acid. The change in the degree of hydrolysis with variation in the value of the concentration of the salt and of the dissociation constant of the acid is illustrated in Table CIX. The values in this table refer to 23.6°, at which temperature the ionic product of water is equal to  $1 \times 10^{-14}$ .

*Mutatis mutandis*, the foregoing discussion applies equally well to the salts of strong acids and weak bases, in which case the hydroxyl ions of the water unite with the cations of the base to form the undissociated molecules of the base. Although the hydrolytic constant represents the ratio  $K_w:K_a$  or  $K_w:K_b$ , it can be derived directly from the law of

mass action without any knowledge of the theory of electrolytic dissociation. The physical significance of the hydrolytic constant is similar to that of the dissociation constant (p. 291), and it may be defined as representing one-half that concentration at which the salt is 50 per cent hydrolyzed, or, if the degree of hydrolysis is small, its square root may be defined as representing the concentration of the products of hydrolysis in a 1 normal solution of the salt.

TABLE CIX

VARIAION IN THE DEGREE OF HYDROLYSIS WITH THE CONCENTRATION OF THE SALT AND THE STRENGTH OF THE ACID

$K_a =$	$10^{-7}$	$10^{-8}$	$10^{-9}$	$10^{-10}$	$10^{-11}$	$10^{-}$
$\frac{K_w}{K_a} =$	$10^{-7}$	$10^{-6}$	$10^{-5}$	$10^{-4}$	$10^{-3}$	$10^{-}$
$c = 1$	0.0003	0.0010	0.0032	0.0100	0.0311	0.0955
$c = 0.1$	0.0010	0.0032	0.0100	0.0311	0.0955	0.2700
$c = 0.01$	0.0032	0.0100	0.0311	0.0955	0.270	0.618
$c = 0.001$	0.0100	0.0311	0.0955	0.270	0.618	0.916

**Hydrolytic Equilibria.** It is not difficult to understand why hydrolysis comes to a standstill. When the weak ions of the salt unite with the oppositely charged ions of water, the place of the former is taken by an equivalent amount of the other ion of water. Since the value of the ionic product of water must always be maintained, it is evident that, as the concentration of the one ion of water increases, the concentration of the other must become less and less, until finally it is too small to unite with the weak ion of the salt. When this occurs, hydrolysis stops and equilibrium sets in.

In the light of what has just been said, it is clear that the addition of hydroxyl ions (a strong base) must bring about a decrease in the degree of hydrolysis of a salt of a weak acid, and, conversely, that the addition of hydrogen ions (a strong acid) must bring about a decrease in the degree of hydrolysis of a salt of a weak base. In either case, as the presence of a high concentration of hydroxyl or hydrogen ions raises the product of the concentrations of the ions above the value of the ionic product of water, water molecules must form at the expense of the added ion and the hydrogen or hydroxyl ion produced by the dissociation of the weak acid or the weak base. The result is a decrease in the degree of

hydrolysis of the salt. For example, the decrease in the degree of hydrolysis of ferric chloride occasioned by the addition of hydrochloric acid to a solution of the salt may be recognized by the disappearance of the red-brown color of the colloidal ferric hydroxide. Again, the addition of a concentrated solution of sodium hydroxide to a solution of ammonium sulphide is accompanied by the disappearance of the odor of hydrogen sulphide. From equation 6 it is evident that, beside hydrogen and hydroxyl ions, the addition of the undissociated product of hydrolysis must also decrease the degree of hydrolysis of a salt. For example, Bredig<sup>1</sup> showed that the acid reaction of aniline hydrochloride disappears on the addition of an excess of aniline. Since the hydrolysis of a salt of a weak acid is brought to a standstill by the accumulation of the hydroxyl ion, and that of a salt of a weak base by the accumulation of the hydrogen ion, then, because only a very small concentration of the hydroxyl ion can exist in the presence of a large concentration of a weak cation, and only a very small concentration of the hydrogen ion can exist in the presence of a weak anion, it follows that the hydrolysis of a salt of one-sided weakness must be increased by adding to its solution a salt of opposite-sided weakness. Thus, the odor of hydrogen sulphide becomes immediately noticeable on the addition of a solution of ammonium chloride to a dilute solution of sodium sulphide.

According to the foregoing discussion all salts are subject to hydrolysis to a greater or less degree. For a salt of an acid or base having a dissociation constant as small as  $10^{-8}$ , hydrolysis amounts to only 0.32 per cent (see Table CIX) in a 0.1 normal solution. For a salt like ammonium chloride (for ammonium hydroxide,  $K = 2.3 \times 10^{-5}$ ), the degree of hydrolysis in a 0.1 normal solution is only

$$\sqrt{\frac{1}{0.1}} \cdot \frac{1.2 \times 10^{-14}}{2.3 \times 10^{-5}} = 0.72 \times 10^{-4} \quad \text{or} \quad 0.0072 \text{ per cent}$$

at 25°. It is evident, therefore, that noteworthy degrees of hydrolysis are found only in solutions of salts of extremely weak acids or

**Methods for the Determination of Hydrolysis.** Equations 4 and 5 show that the hydrolytic constant may be calculated if any one of the following quantities is known:

1. The degree of hydrolysis =  $x$ .
2. The concentration of hydrogen or hydroxyl ions produced by hydrolysis =  $x\alpha_2$ .
3. The concentration of the weak acid or weak base =  $x\alpha$ .

<sup>1</sup> *Z. physik. Chem.*, **13**, 214 (1894).



4. The osmotic concentration of the hydrolyzed salt =  $xc + c(1-x)(1 + \alpha_1) + xc(1 + \alpha_2)$ .

5. The total concentration of the unhydrolyzed salt =  $c(1-x)$ . In the foregoing,  $\alpha_1$  represents the degree of dissociation of the salt, and  $\alpha_2$  the degree of dissociation of the strong base or the strong acid.

(a) *The Conductance Method.* The degree of hydrolysis of many salts may be determined by means of conductance measurements.

The specific conductance of a solution of a uniunivalent salt, MA, of a strong base and a weak acid is made up of the sum of the specific conductance ( $\kappa'$ ) of the strong base (MOH), and the specific conductance ( $\kappa''$ ) of the unhydrolyzed salt MA, since the specific conductance of the weak acid (HA) may be neglected, inasmuch as it is very small in comparison with the specific conductance of the base or that of the unhydrolyzed salt. If, now,  $c$  represents the total concentration of the salt (MA), and  $x$  the degree of hydrolysis, then, for the strong base,

$$\kappa' = \Lambda'_{\text{MOH}} \frac{xc}{1000} \quad (9)$$

where  $\Lambda'_{\text{MOH}}$  represents the equivalent conductance of the base at the concentration  $c$ . Similarly, for the unhydrolyzed salt,

$$\kappa'' = \Lambda''_{\text{MA}} \frac{(1-x)c}{1000} \quad (10)$$

where  $\Lambda''_{\text{MA}}$  represents the equivalent conductance of the unhydrolyzed salt at the concentration  $c$ . On adding equations 9 and 10, we obtain:

$$\kappa = \kappa' + \kappa'' = \frac{c}{1000} [\Lambda'_{\text{MOH}}x + \Lambda''_{\text{MA}}(1-x)] \quad (11)$$

If  $\Lambda$  represents the apparent equivalent conductance of the solution of hydrolyzed salt, i.e.,

$$\Lambda = \kappa \frac{1000}{c}$$

then

$$\Lambda = [\Lambda'_{\text{MOH}}x + \Lambda''_{\text{MA}}(1-x)] \quad (12)$$

whence

$$x = \frac{\Lambda - \Lambda''_{\text{MA}}}{\Lambda'_{\text{MOH}} - \Lambda''_{\text{MA}}} \quad (13)$$

In order to calculate the degree of hydrolysis, it is necessary, therefore, to know the equivalent conductance of the unhydrolyzed salt ( $\Lambda''_{\text{MA}}$ ), the apparent equivalent conductance of the hydrolyzed salt ( $\Lambda$ ), and

the equivalent conductance of the strong base ( $\Lambda'_{\text{MOH}}$ ), all at a concentration  $c$ . The last two of these quantities may be measured directly; the measurement of the first is attended with more or less difficulty. The equivalent conductance of the unhydrolyzed salt at a concentration  $c$  may be obtained by adding to the solution of the hydrolyzed salt an excess of the undissociated product of hydrolysis, the concentration with respect to the salt being kept constant, and then measuring the conductance of the solution. In this way the degree of hydrolysis may be decreased until it approximates zero, when the conductance will be that of the unhydrolyzed salt.

The method just outlined is also applicable to the salt of a weak acid and a weak base, but the calculation of the degree of hydrolysis is more complicated than when only one of the ions of the salt is weak. The conductance method for the determination of the degree of hydrolysis has a practical value only when the difference between the conductance of the unhydrolyzed salt and that of the solution of the hydrolyzed salt is sufficiently large that an accurate determination of its value is possible.

TABLE CX

VALUES OF HYDROLYTIC CONSTANTS DETERMINED BY THE CONDUCTANCE METHOD

	$V = 32$	64	128	256	512	1024
Aniline hydrochloride	$100x = 2.63$ $\frac{x^2c}{1-x} = 2.22$	3.90 2.50	5.47 2.50	7.68 2.50	10.4 2.38	14.4 $2.38 \times 10^{-5}$
<i>o</i> -Toluidine hydrochloride	$100x = 3.07$ $\frac{x^2c}{1-x} = 3.03$	4.60 3.45	6.52 3.57	9.09 3.57	12.5 3.45	17.3 $3.57 \times 10^{-5}$
<i>m</i> -Toluidine hydrochloride	$100x = 2.33$ $\frac{x^2c}{1-x} = 1.73$	3.51 2.00	4.83 1.92	6.60 1.82	9.03 1.75	12.3 $1.70 \times 10^{-5}$
<i>p</i> -Toluidine hydrochloride	$100x = 1.53$ $\frac{x^2c}{1-x} = 0.74$	2.19 0.76	3.16 0.80	4.34 0.77	5.90 0.72	8.33 $0.74 \times 10^{-5}$
Betain hydrochloride	$100x = \dots$ $\frac{x^2c}{1-x} = \dots$	61.4 1515	72.9 1538	83.4 1640	90.6 1695	94.6 $1613 \times 10^{-5}$

The method gives good results when the degree of hydrolysis is neither very large nor very small, that is, when the dissociation constant of the weak acid or weak base lies between  $10^{-9}$  and  $10^{-12}$ . The method may also be employed to obtain an approximate value of the degree of hydrolysis of the salt of a very weak acid or base ( $K < 10^{-14}$ ).

The conductance method was employed by Bredig,<sup>1</sup> Zawidski,<sup>2</sup> and others to determine the degrees of hydrolysis of several salts of weak bases. Some of the results of Bredig's measurements, which were carried out at 25°, are given in Table CX.

(b) *The Determination of the Concentration of the Hydrogen or Hydroxyl Ions.* Of the methods employed to determine the concentration of hydrogen or hydroxyl ions in a solution of a hydrolyzed salt, the following are the more important: catalytic methods, the electromotive-force method, and the colorimetric method. The last method will be discussed in Chapter XXI.

Catalytic methods constitute a very important means of determining the extent to which salts hydrolyze in aqueous solution. These methods depend upon the fact that certain reactions are accelerated by hydrogen or hydroxyl ions, and that the velocity constant of such reactions is proportional to the concentration of these ions. By measuring the velocity constant ( $k_0$ ) of the reaction in the presence of a known concentration of hydrogen or hydroxyl ions (hydrochloric acid or sodium hydroxide), and then the velocity constant ( $k$ ) of the reaction in the presence of salt having the same concentration, it is possible to calculate the degree of hydrolysis and the hydrolytic constant of the salt from the data obtained. Since the ratio

$$\frac{k}{k_0} = x$$

it follows that the

$$\text{Hydrolytic constant} = \frac{\left(\frac{k}{k_0}\right)^2 c}{1 - \frac{k}{k_0}} \quad (14)$$

This method was first employed by Walker,<sup>3</sup> and later by Wood,<sup>4</sup> Lundén,<sup>5</sup> Johnston,<sup>6</sup> and others. In Table CXI are given values of the

<sup>1</sup> *Z. physik. Chem.*, **13**, 289 (1894).

<sup>2</sup> *Ber.*, **36**, 3325 (1903).

<sup>3</sup> *Z. physik. Chem.*, **4**, 319 (1889).

<sup>4</sup> *J. Chem. Soc.*, **83**, 568 (1903).

<sup>5</sup> *Z. physik. Chem.*, **54**, 532 (1906).

<sup>6</sup> *Ibid.*, **57**, 557 (1907).

TABLE CXI

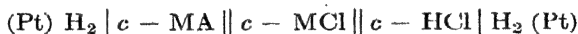
HYDROLYTIC CONSTANTS OF CHLORIDES OF WEAK BASES

Chloride of:	Hydrolytic Constant
Thiourea	10.5
Propionitrile	6.7
Acetamide	4.0
Urea	0.78
Acetoxime	0.0196
Thiohydantoin	0.0127
Asparagine	0.0079
Glycocoll	0.00425
Thiazole	0.00367

hydrolytic constants of a number of chlorides of weak bases, which have been calculated from data obtained by Walker.

On account of the influence of neutral salts, the degree of hydrolysis can be determined with an accuracy of only 1-2 per cent by this method. It is evident, therefore, that good results will be obtained only when the degree of hydrolysis is neither too small nor too large (between 10 and 90 per cent). Consequently, the method may be employed with salts of acids or bases having dissociation constants between  $10^{-10}$  and  $10^{-14}$ .

The hydrogen-ion concentration ( $C_{H^+}$ ) in a solution of a salt, MA, having a total concentration  $c$ , and hence the degree of hydrolysis of salts of weak acids or weak bases, may be found from the electromotive force of the cell



as previously described (p. 216). Since for a salt of a weak acid,

$$x c \alpha_2 = [OH^-] = \frac{K_w}{C_{H^+}}$$

then

$$x = \frac{K_w}{C_{H^+} \cdot c \alpha_2} \quad (15)$$

where  $\alpha_2$  is the degree of dissociation of the base. For a salt of a weak base, we have simply

$$x = \frac{C_{H^+}}{c \alpha_2} \quad (16)$$

The electromotive-force method was used with successful results by Denham<sup>1</sup> to determine the degree of hydrolysis of aniline hydrochloride,

<sup>1</sup> *J. Chem. Soc.*, **93**, 41, 424, 833 (1908)

ammonium chloride, and a number of metal salts, and by Menzel<sup>1</sup> to study hydrolytic equilibria in solutions of salts of carbonic and boric acids.

(c) *The Determination of the Concentration of the Weak Acid or the Weak Base.* These concentrations may be ascertained by distribution measurements.

Suppose that the hydrolysis



takes place, and that the aqueous solution of the hydrolyzed salt is shaken up with a non-miscible solvent, in which, say, the free base is soluble, but not the free acid or the salt. Further, let:

$c_1$  = the total concentration of the salt in the aqueous solution before the addition of the second solvent.

$c_2$  = the concentration of the free base in the second solvent at equilibrium.

$c_3$  = the concentration of the free base in the aqueous solution at equilibrium.

$\delta$  = the distribution coefficient of the free base between water and the second solvent.

$V_2$  = the number of liters of the second solvent employed per liter of aqueous solution.

When equilibrium is established between the two liquid phases,

$$c_3 = \frac{c_2}{\delta} \text{ equivalents per liter} \quad (17)$$

The total concentration (free and combined) of base in the aqueous solution before the addition of the second solvent is  $c_1$ , but, of this amount,  $V_2$  liters of the second solvent extract  $c_2 V_2$  equivalents. Therefore, when equilibrium is established between the two solutions, the total concentration of base in the aqueous solution is

$$c_1 - c_2 V_2 \text{ equivalents per liter}$$

Since, from equation 17, the concentration of free base in the aqueous solution at equilibrium is  $c_2/\delta$  equivalents per liter, it follows that the concentration of unhydrolyzed salt in the aqueous solution at equilibrium is

$$c_1 - c_2 V_2 - \frac{c_2}{\delta} \text{ equivalents per liter}$$

<sup>1</sup> *Z. physik. Chem.*, **100**, 276 (1922).

Then, because none of the acid or salt is extracted from the aqueous solution by the second solvent, the total concentration (free and combined) of acid in the aqueous solution must be equal to the concentration of the salt originally present, i.e., equal to  $c_1$ . Of this amount,

$$c_1 - c_2 V_2 - \frac{c_2}{\delta} \text{ equivalents per liter}$$

are combined in the unhydrolyzed salt. Therefore, there must exist free in the aqueous solution

$$c_1 - \left( c_1 - c_2 V_2 - \frac{c_2}{\delta} \right) = c_2 V_2 + \frac{c_2}{\delta} \quad (18)$$

equivalents per liter. On substituting the foregoing values in equation 6, we obtain

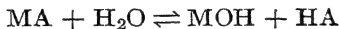
$$\frac{\left( c_2 V_2 + \frac{c_2}{\delta} \right) \left( \frac{c_2}{\delta} \right)}{c_1 - c_2 V_2 - \frac{c_2}{\delta}} = \text{Hydrolytic constant} \quad (19)$$

To determine the hydrolytic constant of a salt by the distribution method, it is first necessary to determine the distribution coefficient of the acid or base between water and the second solvent, and then to determine the quantity of acid or base which passes into the second solvent, when the aqueous solution of the salt is shaken up with it. This method was studied by Farmer<sup>1</sup> and Löfman.<sup>2</sup>

(d) *Determination of the Osmotic Concentration of Hydrolyzed Salt.* Owing to an increase in the number of molecules present in solution, the osmotic pressure of a salt which undergoes hydrolysis must be greater than the calculated value. If the concentration of a binary salt is  $c$  moles per liter, the osmotic concentration ( $C$ ) of the solution is

$$C = (1 - \alpha)c + 2\alpha c = c(1 + \alpha) \quad (20)$$

where  $\alpha$  is the degree of dissociation of the salt. If, however, the salt is one which undergoes hydrolysis, then the osmotic concentration in aqueous solution must be greater than that given by equation 20, for

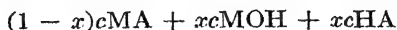


Let us suppose that MA is a salt of a weak acid and a strong base, and let  $\alpha_1$  and  $\alpha_2$  represent the degrees of dissociation of the salt and the base,

<sup>1</sup> *J. Chem. Soc.*, **79**, 863 (1901); **85**, 1713 (1904).

<sup>2</sup> *Z. anorg. Chem.*, **107**, 241 (1919).

respectively, at a concentration  $c$ . Then, since at equilibrium there exist in solution



it is evident that the osmotic concentration of such a solution is

$$C = (1 - x)c(1 + \alpha_1) + xc(1 + \alpha_2) + xc \quad (21)$$

or, since we may assume that  $\alpha_1 = \alpha_2 = \alpha$ ,

$$C = xc + (1 + \alpha)c \quad (22)$$

For an aqueous solution of an unhydrolyzed salt, the freezing-point lowering is  $\Delta = 1.86^\circ \times C$ . Consequently, for an aqueous solution of an unhydrolyzed salt,

$$\Delta = 1.86^\circ [xc + (1 + \alpha)c] \quad (23)$$

On substituting in this equation the value of  $\alpha$  corresponding to a total concentration  $c$  of the salt, the degree of hydrolysis may be calculated from the lowering of the freezing point.

The foregoing method, which is useful for the study of hydrolysis when the degree of hydrolysis is above 40 per cent, was employed by Walden<sup>1</sup> to determine the hydrolysis of dimethylpyron, by Zawidski<sup>2</sup> for the measurement of the hydrolysis of salts of urea, and by Jellinek and Czerwinski<sup>3</sup> to study the hydrolysis of sodium sulphide.

(e) *The Determination of the Total Concentration of the Unhydrolyzed Salt.* It is evident that, if the concentration of the unhydrolyzed portion of a salt can be determined, the extent of its hydrolysis may be readily calculated. This may be accomplished by means of solubility measurements, as Löwenherz<sup>4</sup> showed. The method and calculations are complicated, and they will not be discussed here.

**Hydrolysis of Salts of Weak Acids and Weak Bases.** So far we have confined our discussion to the hydrolysis of salts of a weak acid or weak base—to salts of one-sided weakness. It must be evident, however, that, if a salt is composed of a weak acid and a weak base, its degree of hydrolysis will be greater than if only one of its constituents were weak, for then hydrolysis would proceed much further before the product of the concentrations of the hydrogen and hydroxyl ions reached the value of the ionic product of water.

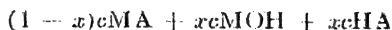
<sup>1</sup> *Ber.*, **34**, 4185 (1901).

<sup>2</sup> *Ibid.*, **37**, 2289 (1904).

<sup>3</sup> *Z. physik. Chem.*, **102**, 433 (1922).

<sup>4</sup> *Ibid.*, **25**, 385 (1898).

In order to derive a relation for the hydrolytic constant of a salt of two-sided weakness, let us consider a solution of a salt (MA) of a weak acid and a weak base, and let the degree of hydrolysis of the salt be  $x$  and its total concentration  $c$ . Then, when equilibrium is established, there will be in solution



Further, the equilibria expressed by the following equations exist in a solution of the salt:

$$\frac{[\text{M}^+][\text{OH}^-]}{[\text{MOH}]} = \frac{[\text{OH}^-](1-x)c}{xc} = K_b \quad (24)$$

$$\frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{[\text{H}^+](1-x)c}{xc} = K_a \quad (25)$$

$$[\text{H}^+][\text{OH}^-] = K_w \quad (26)$$

On multiplying equation 24 by equation 25, and substituting the value of the ionic product of water given in equation 26, we obtain

$$[\text{H}^+][\text{OH}^-] \left( \frac{(1-x)c}{xc} \right)^2 = K_w \left( \frac{(1-x)c}{xc} \right)^2 = K_a K_b \quad (27)$$

or

$$\begin{aligned} \left( \frac{x}{(1-x)} \right)^2 &= \frac{(\text{Concn. acid})(\text{Concn. base})}{(\text{Concn. unhydrolyzed salt})^2} \\ &= \frac{K_w}{K_a K_b} = \text{Hydrolytic constant} \end{aligned} \quad (28)$$

On solving equation 27 for  $x$ , we get

$$x = \frac{1}{1 + \sqrt{\frac{K_a K_b}{K_w}}} \quad (29)$$

Equation 29 shows that the degree of hydrolysis of a salt of two-sided weakness is independent of the concentration, and that it becomes equal to unity only when one of the dissociation constants is equal to zero, that is, when either the acid or base is practically devoid of acidic or basic properties. Under such conditions the salt is incapable of existence in aqueous solution. For this reason the hydroxide is precipitated when ammonium sulphide is added to a solution of a chromium or an aluminium salt.



**The Determination of the Degree of Hydrolysis of a Salt of Two-Sided Weakness.** Arrhenius<sup>1</sup> showed that the degree of hydrolysis of a salt of two-sided weakness, such as aniline acetate, can be obtained approximately as follows: If, for example, it is known that at a dilution of 50 liters the apparent equivalent conductance of aniline acetate is 31.4, then it may be supposed, as a first approximation, that this conductance is due solely to the salt (and that the dissociated portions of aniline and acetic acid may be neglected). Since the conductances of the cation and the anion of aniline acetate are 35 and 43, respectively, at 25°, its equivalent conductance at zero concentration is 78. Hence, only  $31.4/78 = 0.402$  mole of aniline acetate is dissociated at the above-mentioned dilution. Further, it may be supposed that the degree of dissociation of aniline acetate is equal to that of sodium acetate at the same dilution. Consequently, for a concentration of 0.402 mole in 50 liters, this degree of dissociation is equal to 0.91. From this it follows that the total number of dissociated and undissociated moles of aniline acetate is equal to

TABLE CXII  
HYDROLYSIS OF ANILINE ACETATE

V	100x
12.5	54.6
25	55.8
50	56.4
100	55.1
200	55.6
400	55.4
800	56.9
Mean: 55.7	

$0.402/0.91 = 0.442$  mole. Accordingly,  $1 - 0.442 = 0.558$  mole of aniline acetate must have hydrolyzed into aniline and acetic acid. Although the conductance of 0.558 mole of aniline at a dilution of 50 liters is negligible in comparison with that of 0.402 mole of aniline acetate, the conductance of the 0.558 mole of acetic acid is equivalent to that of 0.006 mole of dissociated aniline acetate. Therefore, the apparent equivalent conductance of the solution is due to  $0.402 - 0.006 = 0.396$  mole of dissociated aniline acetate and 0.558 mole of acetic acid. Assuming that the degree of dissociation of aniline acetate at a concentration of 0.396 mole in 50 liters is 0.91, then there must be in the solution 0.396 mole of dissociated and 0.04 mole of undissociated aniline acetate, making a total of 0.436 mole. Hence there must also be present in

<sup>1</sup> *Z. physik. Chem.*, **5**, 18 (1890).

solution 1 — 0.436 = 0.564 mole each of aniline and acetic acid, from which it is evident that the degree of hydrolysis of aniline acetate at a dilution of 50 liters is 0.564.

The values of the degree of hydrolysis of aniline acetate in Table CXII were calculated by Arrhenius by the method just described. In accordance with equation 29, it will be observed that the degree of hydrolysis of aniline acetate does not change appreciably with concentration.

**The Influence of Temperature on Hydrolysis.** In their work on the determination of the ionic product of water, Noyes <sup>1</sup> and his co-workers, Kato and Sosman, investigated the influence of temperature on hydrolysis. The results of their investigations, which were carried out with ammonium acetate, show that the hydrolysis of this salt, at least, increases rapidly as the temperature rises. That this increase is due, in part at least, to an increase in the value of the ionic product of water is evident from equation 29. In Table CXIII are given the results obtained by these investigators with a 0.01 normal solution of ammonium acetate.

TABLE CXIII

INFLUENCE OF TEMPERATURE ON HYDROLYSIS

Temperature	Percentage Hydrolysis
	100x
18°	0.35
100°	4.8
156°	18.3
218°	52.7
306°	91.5

**Reactions of Salts.** Whether a solution of a neutral salt gives an acid or alkaline reaction will depend upon whether the solution contains an excess of hydrogen or hydroxyl ions. When the concentrations of these ions are equal, i.e., when

$$\frac{[\text{H}^+]}{[\text{OH}^-]} = 1$$

the solution must give a neutral reaction. By dividing equation 25 by equation 24, we find that

$$\frac{[\text{H}^+]}{[\text{OH}^-]} = \frac{K_a}{K_b} \quad (30)$$

<sup>1</sup> *J. Am. Chem. Soc.*, **32**, 159 (1910).

Therefore, a neutral reaction is given by a solution of a neutral salt when

$$\frac{K_a}{K_b} = 1 \quad (31)$$

This is approximately the case with a solution of ammonium acetate. Similarly, a solution of a neutral salt gives an acid reaction when

$$\frac{K_a}{K_b} > 1 \quad (32)$$

and an alkaline reaction when

$$\frac{K_a}{K_b} < 1 \quad (33)$$

### PROBLEMS

1. At 25°, the dissociation constant of hydrocyanic acid is  $1.3 \times 10^{-3}$ , and the ionic product of water is  $1.2 \times 10^{-14}$ . Calculate the hydrolytic constant of potassium cyanide, and the degree of hydrolysis of the salt in a 0.01 normal solution.

2. At 25°, the degree of hydrolysis of potassium phenolate is 0.03 in a 0.1 normal solution. Calculate the hydrolytic constant of the salt, and its degree of hydrolysis in a 0.001 normal solution.

3. At a dilution of 512 liters, aniline hydrochloride is 10.4 per cent hydrolyzed at 25°. Calculate the concentration of the hydrogen ions in the solution, assuming that the hydrochloric acid is completely dissociated.

4. At 25°, and at a dilution of 32 liters, the equivalent conductance of *ortho*-toluidine hydrochloride is 98.5, and that of hydrochloric acid at the same concentration is 383. By adding successive small quantities of *ortho*-toluidine to the solution of the hydrochloride (the concentration with respect to the salt being kept constant), the equivalent conductance can be reduced to 89.7, but no further. From these data, calculate the degree of hydrolysis of *ortho*-toluidine hydrochloride at 25°.

5. At 25°, and at a dilution of 64 liters, the specific conductance of betain hydrochloride is  $4.266 \times 10^{-3}$  mho, and that of hydrochloric acid at the same concentration is  $5.984 \times 10^{-3}$  mho. By adding successive small quantities of betain to the solution of the hydrochloride (the concentration with respect to the salt being kept constant), the specific conductance can be reduced to  $1.609 \times 10^{-3}$ , but no further. From these data, calculate (a) the hydrolytic constant of betain hydrochloride, and (b) the degree of hydrolysis of the salt in a 0.01 normal solution.

6. At 25°, the velocity constant of the decomposition of methyl acetate by normal hydrochloric acid is 0.00315, and that by normal thiourea hydrochloride is 0.00290. Calculate the degree of hydrolysis of the salt in a normal solution, and its hydrolytic constant.

7. From the value of the hydrolytic constant obtained in the preceding problem, calculate the dissociation constant of thiourea, being given that the ionic product of water is  $1.2 \times 10^{-14}$  at 25°. At what concentration is thiourea 1 per cent hydrolyzed?

8. Calculate the electromotive force of the cell



being given that the degree of hydrolysis of sodium acetate in 0.001 normal solution is 0.001, and that the electrolytes are completely dissociated.

9. The distribution coefficient of *ortho*-toluidine between water and benzene is 13.4 at 25°. In a certain experiment, a liter of 0.3149 normal *ortho*-toluidine hydrochloride was shaken up with 59 cc of benzene. After equilibrium was established, it was found that the base contained in 50 cc of the benzene layer corresponded to 0.1589 gram of the hydrochloride. With these data, calculate (a) the concentration of the unhydrolyzed salt in the aqueous solution, and (b) the hydrolytic constant of the salt.

10. From the results obtained in the preceding problem, calculate the degree of hydrolysis of the salt, and the concentration of the hydrogen ions in a 0.05 normal solution.

11. The solubility of calcium carbonate in aqueous solution is  $1.5 \times 10^{-3}$  gram per liter. Calculate the degree of hydrolysis of this salt in a saturated solution, assuming that it is hydrolyzed to  $\text{Ca}(\text{HCO}_3)_2$  and being given that the second dissociation constant of  $\text{H}_2\text{CO}_3$  is  $5.4 \times 10^{-11}$ .

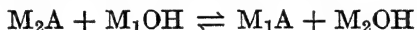
12. The potassium salt of a very weak monobasic acid saponifies methyl acetate 3.17 times as fast when the concentration of the salt is 0.1 *N* as when it is 0.01 *N*. Given that the ionic product of water is  $0.7 \times 10^{-14}$  at the same temperature, calculate the dissociation constant of the acid.

## CHAPTER XX

### THE AVIDITY OF ACIDS AND BASES

The phenomenon of hydrolysis discussed in the preceding chapter is fundamentally only a special case of a general equilibrium problem: the distribution of an acid between two bases, or of a base between two acids. Determination of the manner in which this distribution takes place is of importance in ascertaining the relative strengths—or the avidities—of acids and bases. The term **avidity** was first employed by Thomsen to denote the ability of an acid to obtain possession of a base.

If one equivalent of an acid is mixed with one equivalent of each of two bases, the fraction of the stronger base neutralized by the acid will be larger than that of the weaker base; and the ratio of these fractions will be greater, the greater the difference between the strengths of the two bases. If instead of bringing together one equivalent of an acid and one equivalent of each of two bases, an equivalent of a base ( $M_1OH$ ) is mixed with an equivalent of a salt ( $M_2A$ ) of another base, it is obvious that a certain amount of the base contained in the salt will be displaced by the free base, and that finally the equilibrium



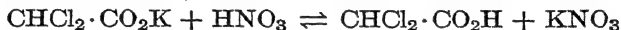
will be established. The greater the avidity of the base  $M_1OH$ , as compared to the base  $M_2OH$ , the greater will be the displacement of the equilibrium in favor of the formation of the salt  $M_1A$ . The position of the equilibrium represents, then, a measure of the ratio of the avidities of the two bases. This conclusion is true, however, only when all the products of reaction remain in solution, that is, when none of the products is volatile or insoluble.

**Experimental Methods for the Determination of Avidity.** Since the application of chemical methods would disturb the composition of the solution at equilibrium, it is generally necessary to determine the position of equilibrium by physical chemical means. Several years before the formulation of the theory of electrolytic dissociation, the avidities of acids and bases had been measured by Ostwald and Thomsen by independent methods. Ostwald<sup>1</sup> investigated the problem by a dilatometric method; Thomsen<sup>2</sup> by a thermochemical method.

<sup>1</sup> *J. prakt. Chem.*, (2) 18, 328 (1878).

<sup>2</sup> *Thermochem. Untersuchungen*, 1882.

(a) *The Dilatometric Method.* Ostwald's dilatometric method is based on the fact that the union of acids and bases is usually accompanied by a change in volume. Thus, when 1000 cc of a normal solution of potassium hydroxide is mixed with an equal volume of normal nitric acid, the volume of the mixture is not 2000 cc but 2020.0 cc. If, on the other hand, 1000 cc of a normal solution of dichloroacetic acid is mixed with an equal volume of potassium hydroxide of the same concentration, the increase in volume is 12.9 cc. Therefore, in the reaction



complete displacement of dichloroacetic acid from a gram equivalent of potassium dichloroacetate would be accompanied by an increase in volume of  $20.0 - 12.9 = 7.1$  cc. If none of the dichloroacetic acid were displaced, there would be no increase in volume. Since Ostwald found that an increase in volume of 5.47 cc resulted on mixing a liter of normal potassium dichloroacetate with an equal volume of normal nitric acid,

it is evident that equilibrium is not established until  $\frac{5.47}{7.1} \times 100 = 77$

per cent of the dichloroacetic acid is displaced from the salt. This means that potassium hydroxide distributes itself between nitric and dichloroacetic acids in the ratio of about 3.4 : 1; or that the avidity of nitric acid is about 3.4 times that of dichloroacetic acid.

The results of Ostwald's measurements are given in Table CXIV. One liter of solution containing a gram equivalent of the first-named acid

TABLE CXIV

THE DISTRIBUTION OF BASES BETWEEN ACIDS

Acids	Potassium Hydroxide	Sodium Hydroxide	Ammonium Hydroxide	Mean
Nitric : dichloroacetic	77	77	75	76
Hydrochloric : dichloroacetic	74	75	73	74
Trichloroacetic : dichloroacetic	70	71	72	71
Lactic : dichloroacetic	8	9	11	9
Trichloroacetic : monochloroacetic	92	92	92	92
Trichloroacetic : formic	97	96	97	97
Lactic : formic	43	46	48	46
Acetic : formic	25	23	23	24
Butyric : formic	21	21	19	20
Isobutyric : formic	19	19	18	19
Acetic : butyric	54	52	53	53
Acetic : isobutyric	56	51	53	53
Formic : propionic	78	80	79	79
Formic : glycollic	43	44	45	44

was added to a liter of solution containing a gram equivalent of the neutral salt of the second acid; the percentages of base abstracted from the salt by the first acid are given in the following columns of the table. This table shows that the values of the ratios of distribution of potassium, sodium, and ammonium hydroxide between any two acids are practically constant within the limits of experimental error. From this it may be concluded that *the relative avidity of an acid is independent of the nature of the base.*

(b) *The Thermochemical Method.* The thermochemical method employed by Thomsen depends on the fact that heat is liberated when an acid is neutralized by a base. As we have already seen, when a very dilute solution of an acid is added to an equally dilute solution containing an equivalent quantity of a base, the heat evolved is independent of the nature of the acid and the base. In more concentrated solutions, however, the heat of neutralization depends to some extent on the nature of the substances.

When one mole of sulphuric acid in about 0.25 normal solution is neutralized by an equivalent quantity of sodium hydroxide of about the

TABLE CXV  
RELATIVE AVIDITIES OF ACIDS

Acid	Relative Avidity
Nitric	100
Hydrochloric	100
Hydrobromic	89
Hydriodic	79
Sulphuric	49
Trichloroacetic	36
Orthophosphoric	25
Oxalic	24
Monochloroacetic	9
Acetic	3

same concentration, the heat developed amounts to 31,380 calories. If the same quantity of sodium hydroxide is neutralized by nitric acid, the heat developed amounts to only 27,360 calories. Suppose, now, that to a solution containing one mole of sodium sulphate an equivalent amount of nitric acid were added. Evidently if all the sulphuric acid were displaced from the salt, there would be an absorption of heat amounting to  $31,380 - 27,360 = 4020$  calories, while if none of the sulphuric acid were displaced from the salt, there would be no heat change. If part of the sulphuric acid were displaced, as is the case, the amount of heat absorbed would lie between zero and 4020 calories. If it may be assumed

that the quantity of acid displaced from the salt is proportional to the amount of heat absorbed, then we are in a position to determine the relative avidities of sulphuric and nitric acids. By means of this method, the relative avidities of a number of acids were determined by Thomsen. Some of his results are given in Table CXV.

(c) *The Determination of Avidity by Other Methods.* Since the avidities of acids of equal concentrations are proportional to the concentration of their hydrogen ions, the relative values of these avidities may be determined by any of the methods previously mentioned for ascertaining hydrogen-ion concentrations. In Table CXVI the relative avidities of a

TABLE CXVI

COMPARISON OF RELATIVE AVIDITIES OF ACIDS OBTAINED BY DIFFERENT METHODS

Acid	Method				
	Thermo-chemical	Dilato-metric	Electro-lytic Conduct-ance	Catalytic Decompo-sition of Methyl Acetate	Inversion of Cane Sugar
Nitric.....	100	100	99.6	92	100
Hydrochloric.....	100	98	100	100	100
Hydrobromic.....	89	.....	101	98	111
Sulphuric.....	49	.....	65	74	73
Trichloroacetic....	36	80	62	68	73
Orthophosphoric..	25	.....	7	.....	6
Oxalic.....	24	.....	20	17	18
Monochloroacetic..	9	7	5	4	5
Tartaric.....	5	5	2.3	2.3	.....
Citric.....	5	.....	1.7	1.6	1.7
Acetic.....	3	1.2	0.4	0.3	0.4

number of the more common acids, determined by different methods, are compared.

**Bases.** What has been said regarding the avidity of acids is true, of course, *mutatis mutandis*, of the avidity of bases.

**Calculation of the Distribution Ratios of Acids and Bases.** Since the avidity of an acid or a base is proportional to its hydrogen- or hydroxyl-ion concentration, and since this in turn is proportional to the dissociation constant of the acid or the base, it is possible with our present



knowledge to calculate the ratio in which a base is distributed between two acids, or an acid is distributed between two bases. In order to do this, let us consider a liter of solution containing:

$c$  moles of a salt  $MA_1$  of a strong base

$c$  moles of an acid  $HA_2$

If we represent by  $x$  the fraction of each mole of the base that remains in combination with the first acid ( $HA_1$ ), and by  $1 - x$  the fraction of each mole of the base taken by the second acid ( $HA_2$ ), then, when equilibrium is reached, there will be in the solution:

$cx$  moles of the salt  $MA_1$

$c(1 - x)$  moles of the salt  $MA_2$

$c - cx$  moles of the acid  $HA_1$

$c - c(1 - x)$  moles of the acid  $HA_2$

If both acids are weak, and both salts (as is usual) highly dissociated, then

$$[A_1^-] = cx$$

$$[A_2^-] = c(1 - x)$$

$$[HA_1] = c - cx$$

$$[HA_2] = c - c(1 - x)$$

since the acids may be regarded as practically undissociated, on account of the presence of their highly dissociated salts. The values of the dissociation constants,  $K_1$  and  $K_2$ , of the acids are given by the expressions

$$K_1 = \frac{[H^+][A_1^-]}{[HA_1]} = \frac{[H^+]cx}{c - cx} \quad (1)$$

and

$$K_2 = \frac{[H^+][A_2^-]}{[HA_2]} = \frac{[H^+] \cdot c(1 - x)}{c - c(1 - x)} \quad (2)$$

On dividing equation 1 by equation 2, we obtain:

$$\frac{K_1}{K_2} = \frac{[H^+] \cdot cx}{c - cx} \left( \frac{c - c(1 - x)}{[H^+] \cdot c(1 - x)} \right) = \left( \frac{x}{1 - x} \right)^2$$

or

$$\frac{x}{1 - x} = \sqrt{\frac{K_1}{K_2}} \quad (3)$$

Equation 3, which was first derived by Arrhenius,<sup>1</sup> shows that the ratio in which two acids are divided between a base is equal to the square root of the ratio of their dissociation constants. The results obtained with this equation agree fairly closely with the mean of those obtained experimentally by Ostwald, as is shown by the data given in Table CXVII.

TABLE CXVII  
RELATIVE AVIDITIES OF ACIDS

Acids	Relative Avidity (100x)	
	Observed	Calculated
Nitric : dichloroacetic.....	76	70
Hydrochloric : dichloroacetic.....	74	70
Trichloroacetic : dichloroacetic.....	71	70
Dichloroacetic : lactic.....	91	95
Trichloroacetic : monochloroacetic...	92	92
Trichloroacetic : formic.....	97	96
Formic : lactic.....	54	55
Formic : acetic.....	76	77
Formic : butyric.....	80	79
Formic : isobutyric.....	81	79
Formic : propionic.....	79	80
Formic : glycollic.....	44	54
Acetic : butyric.....	53	53
Acetic : isobutyric.....	53	53

The ratio in which an acid is distributed between two bases is also given by equation 3, but here  $K_1$  and  $K_2$  represent the dissociation constants of the bases.

### PROBLEMS

1. The heat of neutralization of dichloroacetic acid and of nitric acid by sodium hydroxide is  $-14,830$  and  $-13,680$  calories, respectively. When one gram equivalent of nitric acid is added to one gram equivalent of sodium dichloroacetate in moderately dilute solutions, the quantity of heat absorbed is  $855.5$  calories. Calculate the avidity of nitric acid with respect to dichloroacetic acid.

2. The heat of neutralization of monochloroacetic acid and of trichloroacetic acid by sodium hydroxide is  $-14,280$  and  $-13,920$  calories, respectively. When one gram equivalent of trichloroacetic acid is added to one gram equivalent of sodium

<sup>1</sup> *Z. physik. Chem.*, **5**, 1 (1890).

monochloroacetate in dilute aqueous solution, there is a heat absorption of 331 calories. Calculate the percentage of sodium monochloroacetate decomposed.

3. When 1 liter of a normal solution of trichloroacetic acid is mixed with an equal volume of normal potassium hydroxide, the volume of the mixture is 2017.357 cc. When monochloroacetic acid is substituted for trichloroacetic acid, the volume of the mixture is 2010.885 cc. When 1 liter of a normal solution of trichloroacetic acid is added to an equal volume of normal potassium monochloroacetate, the increase in volume is 5.954 cc. From these data, calculate the avidity of trichloroacetic acid with respect to monochloroacetic acid.

4. At  $25^{\circ}$ , the dissociation constants of formic and acetic acids are  $21.4 \times 10^{-5}$  and  $1.8 \times 10^{-5}$ , respectively. Calculate the percentage of base neutralized by the former acid, when one mole of each of the acids and one mole of sodium hydroxide are brought together in solution.

5. When one mole of dichloroacetic acid and one mole of trichloroacetic acid are present in a liter of solution, the degree of dissociation of the former is one-fifth of the value it would have if it were present alone in the solution. If, in addition to the above quantities of acids, the liter of solution contains one mole of sodium hydroxide, calculate the fraction of the base neutralized by the dichloroacetic acid.

6. When 0.112 normal glycollic acid is mixed with 0.93 normal acetic acid, the degree of dissociation of neither acid changes. Calculate the avidity of glycollic acid with respect to acetic acid.

## CHAPTER XXI

### THE THEORY OF NEUTRALIZATION INDICATORS AND ITS APPLICATION TO VOLUMETRIC ANALYSIS <sup>1</sup>

**The Chemical Nature of Neutralization Indicators.** According to Ostwald,<sup>2</sup> a neutralization indicator is a slightly dissociated organic acid or base which possesses a different color from that of the salt into which it is converted by the addition of alkali or acid. Later investigation showed, however, that this definition was inadequate, and that a neutralization indicator probably always consists of two tautomeric forms (isomers which tend to go over into each other, until equilibrium is reached) possessing different colors, one of which greatly predominates when the indicator exists in the undissociated state, and the other when it exists as a highly dissociated salt. Since it was shown by Noyes<sup>3</sup> that an indicator can be treated in titrations as if it were a single acid or base having a single dissociation constant, we shall consider it as such in the discussion that follows.

**The Requirements to be Fulfilled by a Good Indicator.** Since neutralization indicators are weak acids or weak bases, it is evident that, in the process of neutralization, in the presence of an indicator, we have to deal with the distribution of a base between two acids, of which the indicator acid is one, or with the distribution of an acid between two bases, of which the indicator base is one. Obviously, then, in order to obtain good results in titration, the dissociation constant of the indicator should be small, so that it obtains but a small quantity of the acid or base (see equation 3, Chapter XX). Further, the concentration of the indicator must be small for the same reason. Not only must a good indicator be a *weak* acid or base, but it is essential (1) that the conversion of one tautomeric form into the other must take place instantaneously; (2) that the color change must be wholly due to the conversion of one form into the other; and (3) that the color change must be determined solely by the hydrogen-ion or the hydroxyl-ion concentration, and not by other

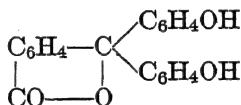
<sup>1</sup> For a more comprehensive presentation of this subject, the reader is referred to Noyes, *J. Am. Chem. Soc.*, **32**, 815 (1910); and to Wegscheider, *Z. physik. Chem.*, **90**, 641 (1915). In this discussion I have followed closely the treatment given by Noyes.

<sup>2</sup> *Lehrbuch*, **1**, 799 (1891).

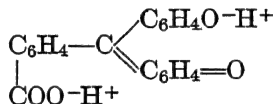
<sup>3</sup> *Loc. cit.*

factors, such as the presence of neutral salts. It is to indicators that fulfill these conditions that the following discussion applies.

Phenolphthalein is an excellent example of a weak acid indicator. In acid solution it is colorless, while in alkaline solution it is intensely red. In acid solution the colorless tautomeric form predominates; in alkaline solution, the red tautomer. The different colors of the tautomers are due to different structures of the molecules. Rosenstein<sup>1</sup> showed that the colorless, or non-dissociating, tautomer has the structure

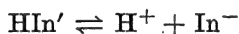


and that the red, or dissociating, tautomer has the structure



If this view is correct, phenolphthalein is a dibasic acid.

**The End Point of Neutralization.** The end point of a titration, in the presence of an indicator acid, is reached when a portion of the non-dissociating tautomer (HIn) changes into the dissociating tautomer (HIn'), which immediately dissociates into its ions:



This point is not perfectly definite, since a certain quantity of base is required to convert the non-dissociating into the dissociating tautomer. The end point of a titration may be defined, however, as being reached when one-half of the non-dissociating tautomer is transformed into the indicator ion, i.e., when

$$[\text{In}^-] = [\text{HIn}] \quad (1)$$

This corresponds to what is done in practice, where frequently the aim is to attain the **neutral color** of the indicator. This color is midway between the **acid color** of the indicator (the color it has in acid solution) and its **alkaline color** (the color it has in alkaline solution). In the case of an indicator acid, the acid color is determined by [HIn] and the alkaline color by [In<sup>-</sup>].

<sup>1</sup> *J. Am. Chem. Soc.*, **34**, 1117 (1912).

**Equilibrium Relations with Reference to the End Point.** Since for an indicator acid the equilibrium relation

$$\frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]} = K_{ia} \quad (2)$$

(where  $K_{ia}$  is the dissociation constant of the indicator acid) must always be fulfilled, in accordance with the definition given above the end point is reached when

$$[\text{H}^+] = K_{ia} \quad (3)$$

It follows from this equation that the end point is determined solely by the hydrogen-ion concentration and, with a particular indicator acid, it is reached when this concentration attains a definite value in the solution being titrated. Obviously, the value of this hydrogen-ion concentration varies with the indicator acid employed. We may conclude from equation 3 that the dissociation constant of any indicator acid is equal to the hydrogen-ion concentration of the solution in which the indicator shows its neutral color.

Similarly, in the case of an indicator base, for which

$$\frac{[\text{In}^+][\text{OH}^-]}{[\text{InOH}]} = K_{ib} \quad (4)$$

the end point of a titration is reached when

$$[\text{OH}^-] = K_{ib} \quad (5)$$

On combining equation 5 with the expression

$$[\text{H}^+][\text{OH}^-] = K_w \quad (6)$$

we find that the end point of a titration, in the presence of an indicator base, is reached when

$$[\text{H}^+] = \frac{K_w}{K_{ib}} \quad (7)$$

Since the end point with an indicator base, like the end point with an indicator acid, is determined by the hydrogen-ion concentration, an indicator base behaves as though it were an indicator acid having a dissociation constant

$$K_{ia} = \frac{K_w}{K_{ib}}$$

Accordingly, hereafter, we shall write  $K_{ia}$  and  $K_w/K_{ib}$  simply  $K_i$ , which we shall call the **indicator constant**. The end point of a titration occurs, then, when the hydrogen-ion concentration becomes equal to the indicator constant, i.e., when

$$[\text{H}^+] = K_i \quad (8)$$

Equation 8 is applicable to either an indicator acid or an indicator base, and when the equation is satisfied the indicator will show its neutral color. Hence, an indicator constant is equal to the hydrogen-ion concentration of a solution in which the indicator gives its neutral color. By making use of this fact, an approximate value of the indicator constant of any indicator can be determined readily, by adding to it a series of solutions of decreasing hydrogen-ion concentration (see Table LX), until its neutral color is produced. The neutral color may be ascertained by superimposing a tube containing a solution of the indicator, in which it shows its acid color, upon one in which the indicator shows its alkaline color.

**The Transformation Color of an Indicator.** Sometimes it is not desirable to take the appearance of the neutral color as the end point of a titration. Thus, with phenolphthalein, the appearance of the first tinge of red when an alkali is added to a solution of an acid containing the indicator is more easily determined than the exact intensity of color corresponding to the conversion of one-half the indicator from the colorless into the colored tautomer. In such cases the end point is indicated by the appearance of what is called the **transformation color** of the indicator. The end point of a titration may be defined more broadly, therefore, as the point at which a definite fraction,  $x$ , of an indicator acid is transformed into its salt,  $\text{MIn}$ ; or the point at which a definite fraction,  $x$ , of the salt,  $\text{InA}$ , of an indicator base is transformed into the free base,  $\text{InOH}$ , the transformation of the indicator being considered always to have taken place in the direction from acid to alkaline, regardless of the direction in which the titration may have actually been made. In what follows, we shall employ this broader definition of the end point. When  $x$  is equal to one-half, the transformation color and the neutral color are identical.

Since, for an indicator acid,

$$\frac{x}{1-x} = \frac{[\text{In}^-]}{[\text{HIn}]}$$

and for an indicator base,

$$\frac{1-x}{x} = \frac{[\text{In}^+]}{[\text{InOH}]}$$

equation 8 may be written in the form

$$[\text{H}^+] = K_i \frac{1-x}{x} = K \quad (8a)$$

The function  $K_i \frac{1-x}{x}$ , or  $K$ , which represents the hydrogen-ion concentration at the end point of a titration, is called the **indicator function**.

In Table CXVIII are given the colors shown by a number of indicators, in the presence of hydrogen ions at different concentrations. Those colors given in heavy type represent the best transformation colors. It is evident from the data given in this table, that indicators may be employed to determine the concentration of hydrogen or hydroxyl ions in solutions. Standard buffer solutions (see Table LX), with well-defined hydrogen-ion concentrations, may be conveniently employed for the colorimetric determination of hydrogen-ion concentrations.<sup>1</sup> The colors given by these solutions with various indicators are compared with those exhibited by the solution under investigation with the same indicators. As already mentioned in Chapter XIX, this colorimetric method may be employed to study the hydrolysis of salts.

**The Error in Titration.** In the neutralization of acids and bases in the presence of an indicator, it is important to know the difference between the quantities of acid and base that must be brought together so that the end point may be reached. The error made in titration depends on this difference. In order to determine this error, let us consider the titration of a monobasic acid HA, against a monacidic base MOH, in the presence of an indicator acid. The error may be determined with the help of the equation

$$[\text{H}^+] + [\text{M}^+] = [\text{A}^-] + [\text{OH}^-] + [\text{In}^-] \quad (9)$$

which expresses the equivalence of the cations and the anions in the solution. Since

$$[\text{H}^+][\text{OH}^-] = K_w$$

it is evident that in equation 9 either the hydrogen- or the hydroxyl-ion concentration is negligible. If, when the end point is reached, the amounts of acid and base brought together are to be equivalent, it follows that in this equation the other of these quantities, hydroxyl- or hydrogen-ion concentration, and the concentration of the indicator ion must also be negligible.

<sup>1</sup> See Clark, *Determination of Hydrogen Ions*, 1928.



TABLE CXVIII

COLORS OF INDICATORS AT DIFFERENT HYDROGEN-ION CONCENTRATIONS

Indicator:	Dimethyl- amino- azobenzene	Methyl Orange	Methyl Red	<i>p</i> -Nitro- phenol	Litmus	Rosolic Acid	Cyanine	Phenol- phthalein	Thymol- phthalein	Trinitro- benzene
Indicator Constant, $K_i$ :	$7 \times 10^{-4}$	$5 \times 10^{-4}$	$1 \times 10^{-5}$	$9 \times 10^{-8}$	.....	$1 \times 10^{-8}$	$2 \times 10^{-9}$	$2 \times 10^{-10}$	$10^{-11}$	.....
Hydrogen-Ion Concentration	Color of Indicator									
$10^{-1}$	Cherry-red	Rose-red	Red	Colorless	Red	Yellow	Colorless	Colorless	Colorless	Colorless
$10^{-2}$	Cherry-red	Rose-red	Red	Colorless	Red	Yellow	Colorless	Colorless	Colorless	Colorless
$10^{-3}$	Fresh color	Rose-red	Red	Colorless	Red	Yellow	Colorless	Colorless	Colorless	Colorless
$10^{-4}$	Golden-yellow	Orange-red	Red	Colorless	Red	Yellow	Colorless	Colorless	Colorless	Colorless
$10^{-5}$	Golden-yellow	Yellow	Pink	Colorless	Red	Yellow	Colorless	Colorless	Colorless	Colorless
$10^{-6}$	Golden-yellow	Yellow	Yellow	Colorless	Red-violet	Yellow	Colorless	Colorless	Colorless	Colorless
$10^{-7}$	Golden-yellow	Yellow	Yellow	Yellow-green	Violet	Yellow	Faint blue	Colorless	Colorless	Colorless
$10^{-8}$	Golden-yellow	Yellow	Yellow	Yellow-green	Blue	Rose	Violet-blue	Colorless	Colorless	Colorless
$10^{-9}$	Golden-yellow	Yellow	Yellow	Yellow-green	Blue	Red	Violet-blue	Rose	Colorless	Colorless
$10^{-10}$	Golden-yellow	Yellow	Yellow	Yellow-green	Blue	Red	Violet-blue	Red	Colorless	Colorless
$10^{-11}$	Golden-yellow	Yellow	Yellow	Yellow-green	Blue	Red	Violet-blue	Red	Colorless	Colorless
$10^{-12}$	Golden-yellow	Yellow	Yellow	Yellow-green	Blue	Red	Violet-blue	Red	Faint-blue	Colorless
$10^{-13}$	Golden-yellow	Yellow	Yellow	Yellow-green	Blue	Red	Violet-blue	Red	Blue	Colorless
$10^{-14}$	Golden-yellow	Yellow	Yellow	Yellow-green	Blue	Red	Violet-blue	Red	Blue	Orange

Suppose that an accuracy of 0.1 per cent in the titration is desired. Then, at the end point, the quantities

$$\frac{[\text{H}^+]}{[\text{A}^-]} = \frac{K}{[\text{A}^-]}, \quad \frac{[\text{OH}^-]}{[\text{A}^-]} = \frac{(K_w/K)}{[\text{A}^-]}, \quad \text{and} \quad \frac{[\text{In}^-]}{[\text{A}^-]}$$

must each be less than 0.1 per cent, or less than  $10^{-3}$ . If, as is often the case, the salt MA has a concentration of  $c = 0.1$  or  $10^{-1}$ , when the end point is reached, then in order to attain the accuracy desired, the value of the indicator function must not be greater than  $10^{-4}$  or less than  $10^{-10}$ . In addition to these limiting values for the indicator function, a maximum limit must be placed on the total concentration of the indicator employed in the titration. Since the fraction of the indicator acid existing as salt is  $x$  when the end point is reached, it is evident that, if the maximum fractional error is to be  $\overline{\text{FE}}$ , the total concentration of the indicator must be less than  $\overline{\text{FE}} \cdot c/x$ , where  $c$  is the total concentration of the salt ( $\text{A}^-$ ) at the end point. In the case of an indicator base, the total concentration of the indicator must not exceed  $\overline{\text{FE}} \cdot c/(1-x)$ . For the case we have just discussed, the concentration of the indicator acid must not exceed  $10^{-4}/x$ .

For an accuracy of 0.1 per cent, under the conditions just outlined, equation 9 becomes

$$[\text{M}^+] = [\text{A}^-] \quad \text{when } K \text{ lies between } 10^{-4} \text{ and } 10^{-10}$$

$$[\text{M}^+] + [\text{H}^+] = [\text{A}^-] \quad \text{when } K \text{ is greater than } 10^{-4}$$

$$[\text{M}^+] = [\text{A}^-] + [\text{OH}^-] \quad \text{when } K \text{ is less than } 10^{-10}$$

If one-half of the indicator is transformed into its salt when the end point is reached, the indicator constant,  $K_i$ , may be substituted for the indicator function,  $K$ , in the above expressions. The foregoing conclusions hold only when the salt formed does not hydrolyze.

**Calculation of the Error Involved in the Titration of Monobasic Acids and Monacidic Bases.** In order to calculate the error involved in the titration of any monobasic acid with any monacidic base, let the total concentration of the acidic constituent in the solution at the end point be  $[\Sigma\text{A}]$  and let that of the basic constituent be  $[\Sigma\text{M}]$ . Evidently,  $V[\Sigma\text{A}]$  and  $V[\Sigma\text{M}]$  (where  $V$  is the volume of the solution) represent the quantities of the acid HA and the base MOH that have been brought together to reach the end point. Further,

$$[\Sigma\text{A}] = [\text{A}^-] + [\text{HA}] + [\text{MA}] \quad (10)$$

and

$$[\Sigma\text{M}] = [\text{M}^+] + [\text{MOH}] + [\text{MA}] \quad (11)$$

An expression for the fractional error made in the titration may be obtained as follows:

On subtracting equation 10 from equation 11, we obtain:

$$[\Sigma M] - [\Sigma A] = [M^+] - [A^-] + [MOH] - [HA] \quad (12)$$

Since it is assumed that the concentration of the indicator ion is negligible, equation 9 may be written

$$[M^+] + [H^+] = [A^-] + [OH^-] \quad (13)$$

On substituting in equation 12 the value of  $[M^+] - [A^-]$  obtained from equation 13, we get

$$[\Sigma M] - [\Sigma A] = [MOH] - [HA] + [OH^-] - [H^+] \quad (14)$$

The dissociation constants of the acid and base used in the titration are given by the expressions

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad (15)$$

and

$$K_b = \frac{[M^+][OH^-]}{[MOH]} \quad (16)$$

On substituting in equation 14 the values of  $[HA]$  and  $[MOH]$  given in equations 15 and 16, we obtain

$$[\Sigma M] - [\Sigma A] = \frac{[M^+][OH^-]}{K_b} - \frac{[H^+][A^-]}{K_a} + [OH^-] - [H^+]$$

or, since

$$[H^+][OH^-] = K_w$$

$$[\Sigma M] - [\Sigma A] = \frac{[M^+]K_w}{[H^+]K_b} - \frac{[H^+][A^-]}{K_a} + \frac{K_w}{[H^+]} - [H^+] \quad (17)$$

On replacing  $[H^+]$  by the indicator function  $K$ , and on putting

$$[M^+] = [A^-]$$

which is permissible so long as their difference is not involved, equation 17 may be written

$$\frac{[\Sigma M] - [\Sigma A]}{[A^-] \text{ or } [M^+]} = \frac{K_w}{KK_b} - \frac{K}{K_a} + \frac{K_w}{K[A^-]} - \frac{K}{[A^-]} \quad (18)$$

Now, if we substitute in equation 10 the value of  $[HA]$  given in equation 15, and replace  $[H^+]$  by  $K$ , we get

$$[\Sigma A] = [A^-] + \frac{K[A^-]}{K_a} + [MA] \quad (19)$$

If  $\alpha_1$  represents the degree of dissociation of the salt  $MA$  in the solution when the end point is reached, equation 19 may be transformed to

$$\begin{aligned} [\Sigma A] &= [A^-] + \frac{K[A^-]}{K_a} + \frac{1 - \alpha_1}{\alpha_1} [A^-] \\ &= [A^-] \left( \frac{1}{\alpha_1} + \frac{K}{K_a} \right) \end{aligned}$$

whence

$$[A^-] = \frac{[\Sigma A]}{\frac{1}{\alpha_1} + \frac{K}{K_a}} \quad (20)$$

Similarly, it may be shown that

$$[M^+] = \frac{[\Sigma M]}{\frac{1}{\alpha_1} + \frac{K_w}{KK_b}} \quad (21)$$

When either the acid or the base is largely dissociated, as is usual in practice, the last term in the denominator of equations 20 and 21 is negligible in comparison with the first. Therefore, under such conditions, these equations become

$$[A^-] = \alpha_1 [\Sigma A] \quad (22)$$

and

$$[M^+] = \alpha_1 [\Sigma M] \quad (23)$$

On substituting the values given in equations 22 and 23 for  $[A^-]$  or  $[M^+]$  in equation 18, we obtain for the fractional error made in the titration of a monobasic acid with a monacidic base the expression

$$\overline{FE} = \frac{[\Sigma M] - [\Sigma A]}{[\Sigma A]} \alpha_1 \left( \frac{K_w}{KK_b} - \frac{K}{K_a} + \frac{K_w}{K_a \alpha_1 [\Sigma A]} - \frac{K}{\alpha_1 [\Sigma A]} \right) \quad (24)$$

So long as  $\overline{FE}$  is moderately small, the normal concentration of the salt in the titrated solution is approximately equal to  $[\Sigma A]$  or  $[\Sigma M]$ . On

replacing  $[\Sigma A]$  by  $c$  and rearranging the terms, equation 24 becomes

$$\overline{FE} = \frac{\alpha_1 K_w}{KK_b} \left( 1 + \frac{K_b}{\alpha_1 c} \right) - \frac{\alpha_1 K}{K_a} \left( 1 + \frac{K_a}{\alpha_1 c} \right) \quad (25)$$

The percentage error is, of course, represented by  $100\overline{FE}$ .

By means of this general equation, the fractional error in the titration of any monobasic acid with any monacidic base can be calculated; and the results are sufficiently accurate for most purposes, even when both the acid and the base are but slightly dissociated. Any difference between the actual and calculated error is due to neglecting the last term in the denominator of equation 20 or 21.

**The Error Involved in the Titration of a Dibasic Acid with a Monacidic Base.** The derivation of an expression for the fractional error involved in this type of titration is somewhat more complicated than in the type just considered, since both the first and second dissociation constants of the dibasic acid must be taken into consideration. Noyes<sup>1</sup> showed that the fractional error is given by the expression

$$\overline{FE} = \frac{\alpha_2 K_w}{KK_b} \left( 1 + \frac{K_b}{\alpha_2 c} \right) - \frac{\alpha_2 K}{2\alpha_1 K_{a_2}} \left( 1 + \frac{2\alpha_1 K_{a_2}}{\alpha_2 c} \right) \quad (26)$$

In this equation  $K_{a_2}$  represents the second dissociation constant of the dibasic acid,  $\alpha_1$  the degree of dissociation of the univalent salt  $MAH$ , and  $\alpha_2$  that of the univalent salt  $M_2A$ .

**Dissociation Constants of Neutralization Acids and Bases.** To facilitate the calculation of titration errors by means of equation 25 or equation 26, values of the dissociation constants of the more important inorganic acids and bases at room temperature are given in Table CXIX.

**Qualitative Rules for the Use of Indicators.** If the indicator employed in a titration is such that its salt undergoes marked hydrolysis, the error made in the titration will be large. Suppose, for example, that we titrate a strong acid with a weak base, such as ammonium hydroxide, and employ phenolphthalein (a weak acid) as the indicator. The appearance of the pink color, which denotes the end point of the titration, depends upon the formation of a definite concentration of the dissociated salt of the indicator and ammonium hydroxide. Since this is the salt of a very weak acid and a weak base—a salt of two-sided weakness—it is evident, in the light of our discussion in Chapter XIX, that it will immediately hydrolyze and that the undissociated indicator will be reformed. Therefore, a permanent pink color will not be obtained until a consider-

<sup>1</sup> *J. Am. Chem. Soc.*, **32**, 815 (1910).

able excess of ammonium hydroxide has been added to the solution. Accordingly, a weak indicator acid should not be employed. For the same reasons, a weak indicator base should not be used in titrating a weak acid. On the other hand, a weak indicator acid must be employed in titrating a weak acid, so that the fraction of the base that combines with the indicator will be small in comparison with that which combines with the weak acid.

TABLE CXIX

## DISSOCIATION CONSTANTS OF ACIDS AND BASES

Acid or Base	Dissociation Constant	
<i>Monobasic Acids</i>	$K_a$	
HCl, HBr, HI	1	
HNO <sub>3</sub> , HClO <sub>3</sub> , HClO <sub>4</sub>	1	
HNO <sub>2</sub>	$5 \times 10^{-4}$	
HClO	$4 \times 10^{-8}$	
HCN	$7 \times 10^{-10}$	
HH <sub>2</sub> BO <sub>3</sub>	$7 \times 10^{-10}$	
HH <sub>2</sub> AsO <sub>3</sub>	$6 \times 10^{-10}$	
<i>Dibasic Acids</i>	$K_{a1}$	$K_{a2}$
H <sub>2</sub> SO <sub>4</sub>	1	$3 \times 10^{-2}$
H <sub>2</sub> CrO <sub>4</sub>	1	$6 \times 10^{-7}$
H <sub>2</sub> SO <sub>3</sub>	$1.7 \times 10^{-2}$	.....
H <sub>2</sub> CO <sub>3</sub>	$3.0 \times 10^{-7}$	$3 \times 10^{-11}$
H <sub>2</sub> S	$9.1 \times 10^{-8}$	$1 \times 10^{-15}$
<i>Monacidic Bases</i>	$K_b$	
KOH, NaOH	1	
( $\frac{1}{2}$ Ba)OH, ( $\frac{1}{2}$ Ca)OH *	0.3	
NH <sub>4</sub> OH	$1.8 \times 10^{-5}$	

\* Since barium and calcium hydroxides apparently do not dissociate in stages with the formation of intermediate ions, they may be regarded as monacidic bases.

In view of what has just been said, it is obvious that the nature of the indicator to be employed in titration depends upon the strength of the acid and base used. Below are given qualitative rules for the kind of indicator to be employed in a number of different titrations:

- With strong acids and bases any indicator may be used.
- With strong acids and weak bases, a strong indicator acid or a weak indicator base should be used.
- With weak acids and strong bases, a weak indicator acid or a strong indicator base should be employed.
- Weak acids should never be titrated against weak bases.

Wegscheider<sup>1</sup> showed that better results may be obtained in titration by the use of an indicator acid that is colored in alkaline solution, or an indicator base that is colored in acid solution, than by the use of an indicator acid that is colored in acid solution, or an indicator base that is colored in alkaline solution.

**The Maximum, Minimum, and Best Values of the Indicator Function.** The best indicator to be employed in cases (b) and (c) depends upon the value of the indicator function, which, as is shown by equation 25, plays an important part in determining the error made in titration. In order to keep this error below a given quantity, it is necessary that the indicator function have a value which lies between a certain "maximum value" and a certain "minimum value." In order to attain the minimum error, it is necessary to secure for the indicator function a value as nearly equal to its "best value" as possible. In Table CXX are given values of the square of the best value, the maximum value, and the minimum value of the indicator function for a number of types of titration.

TABLE CXX

## VALUES OF THE INDICATOR FUNCTION

Titration, with a Largely Dissociated Acid or Base, of:	Square of Best Value	Maximum Value	Minimum Value
A monobasic acid	$10K_wK_a$	$(\overline{FE})K_a$	$10K_w/K_a$
A monacidic base	$0.1(K_w/K_b)$	$0.1(\overline{FE})$	$K_w/\{(\overline{FE})K_b\}$
The total hydrogen of a dibasic acid	$10K_w2K_{a2}$	$(\overline{FE})2K_{a2}$	$10K_w/(\overline{FE})$

As an example of the use of the data in Table CXX, let us suppose that we wish to titrate ammonium hydroxide ( $K_b = 1.8 \times 10^{-5}$ ) against hydrochloric acid ( $K_a = 1$ ) with the least possible error. We find from the table that the square of the best value of the indicator function, for the titration of a monacidic base against a strong monobasic acid, is  $0.1(K_w/K_b) = 10^{-1} \times 10^{-14} \div (1.8 \times 10^{-5})$ . The best value of the indicator function, then, is  $7.45 \times 10^{-6}$ . Reference to Table CXVIII and equation 8a shows that this value may be secured by using methyl red as the indicator, and causing it to be about 58 per cent transformed into its salt at the end point. If an accuracy of 0.1 per cent ( $FE = 10^{-3}$ ) is desired, it is evident from Table CXX that the value of the indicator function must lie between  $10^{-4}$  and  $5.56 \times 10^{-6}$ . This shows that the minimum value of the indicator function lies very close to its best value, and that the maximum value must not be greater than about 14 times the best value.

<sup>1</sup> *Z. physik. Chem.*, **90**, 641 (1915).

## REFERENCE

PRIDEAUX, *Theory of Indicators*.

## PROBLEMS

1. Which of the indicators given in Table CXVIII show their neutral color in a solution which is exactly neutral? A violet-blue color is obtained when a drop of cyanine is added to a certain solution, but the solution remains colorless on the addition of phenolphthalein. What is the approximate concentration of the hydrogen ions in this solution?

2. A certain solution contains 0.001 equivalent of ammonium hydroxide and 0.1 equivalent of ammonium chloride per liter. Assuming that the ammonium chloride is completely dissociated at the above concentration, what will be the color produced on the addition, to separate portions of the solution, of (a) dimethylaminoazobenzene, (b) methyl orange, (c) rosolic acid, (d) phenolphthalein, and (e) trinitrobenzene?

3. How much water must be added to 1 liter of 0.01 normal sodium hydroxide so that the solution on the addition of phenolphthalein will no longer give the alkaline color of the indicator?

4. A 0.1 normal solution of the sodium salt of a monobasic acid gives a rose color with phenolphthalein but remains colorless on the addition of thymolphthalein. Calculate, approximately, the degree of hydrolysis of the salt in the solution, and the dissociation constant of the acid.

5. Calculate the error made in titrating 0.2 normal acetic acid against 0.2 normal potassium hydroxide, using as an indicator (a) methyl orange, and (b) rosolic acid.

6. What is the error made in titrating 0.2 normal sulphuric acid against 0.2 normal sodium hydroxide, when methyl red is used as the indicator?

7. Which of the indicators given in Table CXVIII should be employed in titrating 0.5 normal sodium hydroxide against acetic acid of the same concentration, if the least error is to be involved?

8. What indicators would you recommend for the determination of bicarbonate in the presence of normal carbonate of soda?

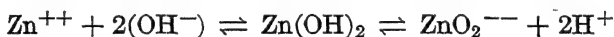


## CHAPTER XXII

### AMPHOLYTES

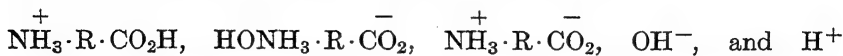
Substances which behave as both acids and bases, that is, substances which possess the ability of forming, or combining with, both hydrogen and hydroxyl ions, are called **ampholytes**. Zinc hydroxide is a familiar example of this type of electrolyte. This substance reacts with hydrochloric acid to form zinc chloride, or with sodium hydroxide to produce sodium zincate. Acidic and basic properties are exhibited by the hydroxides of most of the weakly positive metals, by the oximes, and by the amino acids. In a sense, water itself is an ampholyte, since it yields both hydrogen and hydroxyl ions.

**Ampholytic Dissociation.** The ampholytic dissociation of an electrolyte like zinc hydroxide can be represented by the equation



It is evident from this equation that the addition of a strong base to a solution of the ampholyte must, on account of the mutual ion, retard the production of zinc ions and must also, in consequence of the consumption of hydrogen ions in the formation of water, favor the formation of  $\text{ZnO}_2^{--}$  ions. *Mutatis mutandis*, the addition of a strong acid to the ampholyte must decrease the concentration of the  $\text{ZnO}_2^{--}$  ions and increase that of the zinc ions. Since ampholytes behave like both acids and bases, the dissociation of such substances is governed by two dissociation constants: one,  $K'_a$ , for the acidic dissociation; the other,  $K'_b$ , for the basic dissociation. The law of mass action was first applied to the dissociation equilibria of this type of electrolyte by Bredig,<sup>1</sup> and later, more completely, by Walker.<sup>2</sup>

According to the current view, the dissociation of an amino acid ( $\text{HONH}_3 \cdot \text{R} \cdot \text{CO}_2\text{H}$ ) gives rise to the following ions:



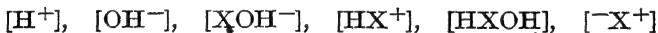
The *Zwitterion*,  $\overset{+}{\text{NH}}_3 \cdot \text{R} \cdot \overset{-}{\text{CO}}_2$ , which is sometimes termed an intramo-

<sup>1</sup> *Z. Elektrochem.*, **6**, 33 (1899).

<sup>2</sup> *Proc. Roy. Soc.*, **73**, 155 (1904); *Z. physik. Chem.*, **49**, 82 (1904); **51**, 706 (1905).

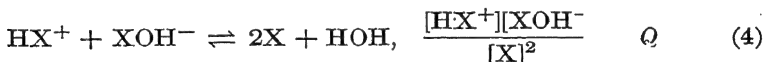
lecular salt, has not been believed to exist in considerable amounts.<sup>1</sup> Since this ion carries equivalent positive and negative charges, it may be regarded as the anhydrous form of the undissociated acid. It may be formed either by the splitting off of water from the ampholyte; by the further dissociation of the ions,  $\text{HONH}_3 \cdot \text{R} \cdot \text{CO}_2^-$  or  $\text{NH}_3 \cdot \text{R} \cdot \text{CO}_2\text{H}^+$ ; or by the splitting off of water from two of these ions.

**Equilibrium Relations of Ampholytes.** In order to determine the equilibrium relations of an ampholyte,  $\text{HXOH}$ , let the concentrations of the various molecular species present at equilibrium be represented as follows:



The undissociated portion of the ampholyte has either the composition  $\text{HXOH}$  or that of the anhydride,  $\text{X}$ . Of the quantities given above, either  $[\text{H}^+]$  or  $[\text{OH}^-]$  is negligible. In consequence of the very small ionic product of water,  $[\text{HX}^+]$  is negligible when  $[\text{OH}^-]$  is large, and  $[\text{XOH}^-]$  is negligible when  $[\text{H}^+]$  is large, since the dissociation constants of an ampholyte are usually small.

The equilibria between the different cations and anions present in the general equilibrium of an ampholyte are expressed by the following equations:



On multiplying equation 2 by equation 3, we obtain:

$$[\text{H}^+][\text{OH}^-][\text{XOH}^-][\text{HX}^+] = K'_a K'_b [\text{HXOH}]^2$$

and on substituting in this expression the values of  $[\text{H}^+][\text{OH}^-]$  and  $[\text{XOH}^-][\text{HX}^+]$  given in equations 1 and 4, we get

$$\frac{[\text{HXOH}]^2}{[\text{X}]^2} = \frac{K_w Q}{K'_a K'_b}$$

from which it is evident that the ratio of  $[\text{HXOH}]$  to  $[\text{X}]$  is constant.

<sup>1</sup> "Zwitterion" structure in organic molecules has been discussed by Weizmann, *Trans. Faraday Soc.*, **36**, 978 (1940).

If we denote the sum of the concentrations of the undissociated forms of the ampholyte by  $S$ , i.e.,

$$S = [\text{HXOH}] + [\text{X}]$$

equations 2 and 3 may be written

$$\frac{[\text{H}^+][\text{XOH}^-]}{S} = K_a \quad (5)$$

and

$$\frac{[\text{HX}^+][\text{OH}^-]}{S} = K_b \quad (6)$$

where  $K_a$  and  $K_b$  are the *apparent* acidic and basic dissociation constants, that is the dissociation constants that can be determined experimentally. The *true* dissociation constants,  $K'_a$  and  $K'_b$ , cannot be calculated from conductance or hydrolysis measurements.

On substituting in equation 5 the value of  $[\text{H}^+]$  given in equation 1, we obtain:

$$[\text{XOH}^-] = \frac{K_a}{K_w} \cdot S \cdot [\text{OH}^-] \quad (7)$$

Similarly,

$$[\text{HX}^+] = \frac{K_b}{K_w} \cdot S \cdot [\text{H}^+] \quad (8)$$

On substituting these values of  $[\text{XOH}^-]$  and  $[\text{HX}^+]$  in the equation

$$[\text{H}^+] + [\text{HX}^+] = [\text{OH}^-] + [\text{XOH}^-] \quad (9)$$

which expresses the equivalence of the cations and the anions, we obtain

$$[\text{H}^+] \left( 1 + \frac{K_b}{K_w} \cdot S \right) = [\text{OH}^-] \left( 1 + \frac{K_a}{K_w} \cdot S \right) \quad (10)$$

By combining this last expression with equation 1 and rearranging the terms, we get

$$[\text{H}^+] = \sqrt{\frac{K_w + K_a \cdot S}{1 + \frac{K_b}{K_w} \cdot S}} \quad (11)$$

Similarly,

$$[\text{OH}^-] = \sqrt{\frac{K_w + K_b \cdot S}{1 + \frac{K_a}{K_w} \cdot S}} \quad (12)$$

These relations show that an ampholyte approaches more and more closely to an ordinary electrolyte, the smaller one of its dissociation constants is, and the smaller its concentration. For ordinary acids ( $K_b = 0$ ) and bases ( $K_a = 0$ ), equations 11 and 12 would be

$$[H^+] = \sqrt{K_w + K_a S} \quad (13)$$

and

$$[OH^-] = \sqrt{K_w + K_b S} \quad (14)$$

**Some Properties of Ampholytes.** From equations 11 and 12, it is evident that the conductance of an ampholyte, when calculated in the usual manner, does not constitute a measure of either the acidity or the basicity, or of the dissociation of the electrolyte. This is due to the fact that the cation  $HX^+$ , in addition to the hydrogen ion, and the anion,  $XOH^-$ , as well as the hydroxyl ion, are present in the solution. The observed equivalent conductance of an ampholyte is equal to the sum of the products of the ionic concentrations and the ion conductances. It follows from equations 7 and 8 that the concentrations of the two anions are equal only when  $K_w/K_a = S$ , and those of the two cations, when  $K_w/K_b = S$ . If the ratio of the dissociated to the undissociated portion of the molecule is small,  $S$  is approximately equal to the total concentration,  $c$ , of the ampholyte. Accordingly, the concentrations of the two cations are equal when  $c$  is approximately equal to  $K_w/K_b$ .

If the acidic and basic characteristics of an ampholyte are about equal, that is, if  $K_a = K_b$ , it follows from equations 11 and 12 that  $[H^+] = [OH^-] = \sqrt{K_w}$ , and that the solution will have a neutral reaction. Neutral ampholytes differ from other electrolytes in that they form salts which hydrolyze to a small extent, even when both dissociation constants are large. In another respect the behavior of such ampholytes is peculiar, on the basis of our theories of electrolytic conductance. Since  $[H^+]$  and  $[OH^-]$  are constant at all concentrations, it follows from equations 5 and 6 that  $[XOH^-]/S$  and  $[HX^+]/S$  are also constant, i.e., the degree of dissociation of the ampholyte is independent of the concentration. If, for example,  $K_a = K_b = 1.2 \times 10^{-7}$ , then from equations 5 and 6 it will be found that  $[XOH^-]/S = [HX^+]/S = 1.1$ , or that the degree of dissociation is 52 per cent at all concentrations. Thus, notwithstanding the fact that the ampholyte is simultaneously an acid 100 times weaker than acetic acid and a base 100 times weaker than ammonium hydroxide, it has a good conductance.

Since the total concentration,  $c$ , of a solution of an ampholyte,  $HXOH$ , is equal to the sum of the concentrations of all the molecular species containing  $X$ , we may write

$$c = S + [XOH^-] + [HX^+] \quad (15)$$

From this expression and equation 9 it follows, when  $[\text{OH}^-]$  is very small, that

$$c = S + [\text{H}^+] + 2[\text{HX}^+] \quad (16)$$

or, when  $[\text{H}^+]$  is very small, that

$$c = S + [\text{OH}^-] + 2[\text{XOH}^-] \quad (17)$$

Hence, if the apparent dissociation constants,  $K_a$  and  $K_b$ , are known, the ionic concentrations,  $[\text{H}^+]$ ,  $[\text{OH}^-]$ ,  $[\text{HX}^+]$ , and  $[\text{XOH}^-]$ , may be calculated by successive approximations. As a first approximation, the concentration  $S$ , of the undissociated molecules, is assumed to be equal to the total concentration,  $c$ , of the ampholyte, and  $[\text{H}^+]$  or  $[\text{OH}^-]$  calculated from equation 11 or 12. An approximate value of  $[\text{HX}^+]$  or  $[\text{XOH}^-]$  is then obtained from equation 8 or 7. With this value,  $S$  may be found from equation 16 or 17, and then a second approximation of  $[\text{HX}^+]$  or  $[\text{XOH}^-]$  may be obtained by solving equation 8 or 7. This method of approximation was employed by Walker<sup>1</sup> to determine the influence of variation in concentration and basic strength on the dissociation of an amphoteric acid. The results of his calculations are given in Table CXXI.

TABLE CXXI

THE DISSOCIATION OF AN AMPHOTERIC ACID

$$K_a = 10^{-5}.$$

(The values of  $[\text{H}^+]$  and  $[\text{HX}^+]$  are multiplied by  $10^5$ .)

$K_b/K_a = 0$			1	10	100	100
$c$	$[\text{H}^+]$	$[\text{HX}^+]$	$[\text{H}^+]$ $[\text{HX}^+]$	$[\text{H}^+]$ $[\text{HX}^+]$	$[\text{H}^+]$ $[\text{HX}^+]$	$[\text{H}^+]$ $[\text{HX}^+]$
1.0	316	0	224 223	95.3 934	31.5 2960	9.99 8330
0.1	100	0	95 9.4	70.5 69.0	30.1 283	9.94 830
0.01	31.2	0	31.0 0.3	29.7 2.9	22.0 20.6	9.44 79
0.001	9.5	0	9.5 0	9.4 0.1	9.06 0.8	6.73 5.5
0.0001	2.7	0	2.7 0	2.7 0.01	2.69 0.02	2.61 0.18

The data in Table CXXI show, for a given concentration, that the hydrogen-ion concentration decreases as the value of the basic dissociation constant increases; and that the concentration of the  $\text{HX}^+$  ions changes more rapidly with dilution than that of the hydrogen ions, the

<sup>1</sup> *Z. physik. Chem.*, **49**, 82 (1904); **51**, 706 (1905).

hydrogen-ion concentration being practically independent of the dilution at the highest value of the basic dissociation constant. Most interesting is the fact that at high concentrations the acidity of an ampholyte is greatly decreased by an increase in the value of the basic dissociation constant, even though the value of the acidic constant is about a million times greater than that of the basic dissociation constant.

**The Apparent Dissociation Constant of an Ampholyte.** In order to obtain an expression for the apparent dissociation constant, let us consider the conductance of an ampholyte whose acidic dissociation constant is much greater than its basic constant. It has already been mentioned that the observed equivalent conductance of such an electrolyte is equal to the sum of the products of the conductances of the ions and their corresponding concentrations. In the solution of the ampholyte we are considering, the hydroxyl-ion concentration is negligible, and we may write:  $[H^+] + [HX^+] = [XOH^-]$ . Accordingly, the specific conductance of the ampholyte is

$$\begin{aligned}\kappa &= \frac{[H^+](\Lambda_{H^+}) + [HX^+](\Lambda_{HX^+}) + [XOH^-](\Lambda_{XOH^-})}{1000} \\ &= \frac{[H^+](\Lambda_{H^+} + \Lambda_{XOH^-}) + [HX^+](\Lambda_{HX^+} + \Lambda_{XOH^-})}{1000} \quad (18)\end{aligned}$$

For organic electrolytes,  $(\Lambda_{H^+} + \Lambda_{XOH^-}) = 370$  to  $380$ , and  $(\Lambda_{HX^+} + \Lambda_{XOH^-}) = 65$  to  $80$ , at  $25^\circ$ , the sum of the latter conductances being about 5 to 6 times smaller than the sum of the former. Accordingly, where  $5 < r < 6$ , equation 18 may be written

$$\kappa = \frac{\left([H^+] + \frac{[HX^+]}{r}\right)(\Lambda_{H^+} + \Lambda_{XOH^-})}{1000} \quad (19)$$

For a simple acid, such as acetic acid,

$$\begin{aligned}\kappa &= \frac{[H^+](\Lambda_{H^+}) + [H^+](\Lambda_{CH_3CO_2^-})}{1000} \\ &= \frac{[H^+](\Lambda_{H^+} + \Lambda_{CH_3CO_2^-})}{1000}\end{aligned}$$

and the dissociation constant is

$$K = \frac{[H^+]^2}{c - [H^+]}$$

Similarly, the apparent dissociation constant,<sup>1</sup>  $K_0$ , of an ampholyte, whose acidic dissociation constant is much greater than its basic constant, is

$$K_0 = \frac{\left( [\text{H}^+] + \frac{[\text{HX}^+]}{r} \right)^2}{- \left( [\text{H}^+] + \frac{[\text{HX}^+]}{r} \right)} \quad (20)$$

Evidently, if the values of  $[\text{H}^+]$  and  $[\text{HX}^+]$  are known, the apparent dissociation constant of an ampholyte may be calculated by means of equation 20. On the other hand, if the value of  $K_0$  can be determined directly from conductance measurements, with the help of the equations

$$\frac{\Lambda}{\Lambda_0} \quad \text{and} \quad \frac{\alpha^2 c}{1 - \alpha} = K_0$$

it may be employed to calculate  $\left( [\text{H}^+] + \frac{[\text{HX}^+]}{r} \right)$ . That the values calculated for the apparent dissociation constant of an ampholyte ( $K_0$  calc.) by means of equation 20 agree closely with those determined directly from conductance measurements ( $K_0$  obs.) is shown by the data for *ortho*-aminobenzoic acid in Table CXXII. The values of  $K_0$  given in the table were measured by Ostwald<sup>2</sup> and calculated by Walker.<sup>3</sup>

TABLE CXXII

THE APPARENT DISSOCIATION CONSTANT OF *ortho*-AMINO-BENZOIC ACID

$$K_b/K_w = 112. \quad K_a = 1.04 \times 10^{-5}. \quad \Lambda = 355.$$

V	$[\text{H}^+] \cdot 10^5$	$[\text{HX}^+] \cdot 10^5$	$\Lambda$ Observed	$K_0 \cdot 10^5$ Calculated	$K_0 \cdot 10^5$ Observed
64	24.0	39.1	7.21	0.66	0.66
128	20.4	16.6	10.8	0.74	0.74
256	16.3	6.6	16.2	0.84	0.84
512	12.4	2.5	23.6	0.92	0.91
1024	9.1	0.89	33.7	0.97	0.97

### The Determination of the Acidic and Basic Dissociation Constants.

A knowledge of the values of the apparent acidic and basic dissociation constants of ampholytes is often important. Two methods are employed

<sup>1</sup> The apparent dissociation constant of an ampholyte must not be confused with the apparent *acidic* dissociation constant  $K_a$ , or the apparent *basic* dissociation constant  $K_b$ .

<sup>2</sup> *Z. physik. Chem.*, **3**, 261 (1889).

<sup>3</sup> *Ibid.*, **49**, 82 (1904); **51**, 706 (1905).

for the determination of these quantities: the conductance and the hydrolytic.

(a) *The Conductance Method.* The larger dissociation constant, say  $K_a$ , of an ampholyte can be calculated from conductance data by means of equations 8, 11, 16, and 20, if the smaller dissociation constant, say  $K_b$ , has been determined previously. We shall see that the smaller dissociation constant can be ascertained by measuring the hydrolysis of a salt of the ampholyte. The conductance method may be employed with good results when the value of the larger dissociation constant is not less than  $10^{-7}$  or  $10^{-8}$ ; otherwise the conductance of the ampholyte is too small to be determined accurately.

The calculation of the larger dissociation constant,  $K_a$ , from conductance data may be best explained by an example. For *ortho*-aminobenzoic acid, it has been found from conductance measurements that the apparent dissociation constant ( $K_0$ ) is  $0.66 \times 10^{-5}$  at  $25^\circ$ , at a dilution of 64 liters. Measurements of the hydrolysis of the chloride of the acid have shown that  $K_b/K_w = 112$ . On solving equation 20, we find that, at a dilution of 64 liters,

$$\left( [\text{H}^+] + \frac{[\text{HX}^+]}{5} \right) = 31.8 \times 10^{-5} \quad (21)$$

On combining this equation with equation 8, and assuming as a first approximation that  $c = S$ , we obtain

$$[\text{HX}^+] = 41.2 \times 10^{-5}$$

from which it follows that

$$[\text{H}^+] = 23.6 \times 10^{-5}$$

From equation 16 it is evident, therefore, that

$$S = 0.01459$$

On substituting this value of  $S$  and that of  $[\text{H}^+]$  in equation 8, we get as a second approximation

$$[\text{HX}^+] = 39.2 \times 10^{-5}$$

On introducing this new value of  $[\text{HX}^+]$  in equation 21, we obtain

$$[\text{H}^+] = 24.0 \times 10^{-5}$$

These are the values of  $[\text{H}^+]$  and  $[\text{HX}^+]$  given in Table CXXII. On substituting the values obtained for  $[\text{H}^+]$ ,  $S$ , and  $K_b$  in equation 11 and solving for  $K_a$ , we find

$$K_a = 1.04 \times 10^{-5}$$

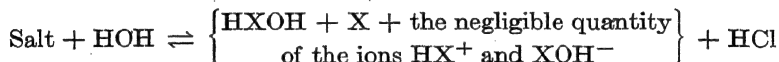


(b) *The Hydrolytic Method.* A small basic (or acidic) dissociation constant (less than  $10^{-9}$ ) of an ampholyte may be determined by the measurement of the hydrolysis of its chloride (or sodium salt). The calculations are made in exactly the same manner as for simple acids and bases. In this method, the larger dissociation constant is neglected while determining the former. Lundén<sup>1</sup> showed, however, that the error introduced by doing this is usually negligible.

Suppose that we have a solution of the chloride,  $\text{HXC}\text{l}$ , of an ampholyte,  $\text{HXOH}$ . When equilibrium is established, the concentrations of the different molecular species in solution may be represented as follows:



The hydrolytic equilibria may be expressed thus:



If  $c$  represents the total concentration of the salt  $\text{HXC}\text{l}$ , and  $x$  its degree of hydrolysis, then at equilibrium the concentration of the unhydrolyzed salt is  $(1 - x)c$  and that of the hydrochloric acid  $xc$ . Since the hydrochloric acid and the salt  $\text{HXC}\text{l}$  are completely dissociated at the concentrations employed in experimental work,

$$[\text{Cl}^-] = c \quad (22)$$

Owing to the presence of hydrochloric acid in the solution of the hydrolyzed salt, the hydroxyl-ion concentration must be so small that the basic dissociation of the ampholyte may be neglected.

Let the hydrogen-ion concentration resulting from the acidic dissociation of  $\text{HXOH}$  be  $\delta$ . This quantity must be equal to the concentration of the  $\text{XOH}^-$  ions derived from the same dissociation. The total hydrogen-ion concentration (derived from the acidic dissociation of  $\text{HXOH}$  and from the hydrolysis of the salt  $\text{HXC}\text{l}$ ), then, is

$$[\text{H}^+] = xc + \delta \quad (23)$$

and that of the  $\text{XOH}^-$  ions

$$[\text{XOH}^-] = \delta \quad (24)$$

Since the only source of  $\text{HX}^+$  ions is the dissociation of the salt  $\text{HXC}\text{l}$ ,

$$[\text{HX}^+] = (1 - x)c \quad (25)$$

<sup>1</sup> *J. Biol. Chem.* **4**, 267 (1908).

The total concentration of the salt is equal to the sum of the concentrations of the substances containing X. Hence

$$c = [\text{XOH}^-] + [\text{HX}^+] + S$$

whence

$$c = \delta + (1 - x)c + S$$

or

$$S = xc - \delta \quad (26)$$

On substituting in equation 8 this value of  $S$  and the values of  $[\text{H}^+]$  and  $[\text{HX}^+]$  given in equations 23 and 25, we obtain for the apparent basic dissociation constant the expression

$$K_b = \frac{K_w(1 - x)c}{(xc + \delta)(xc - \delta)} \quad (27)$$

or

$$\begin{aligned} \frac{K_b}{K_w} &= \frac{(1 - x)c}{(xc + \delta)(xc - \delta)} \\ &= \frac{1 - x}{x^2c} \cdot \left[ \frac{1}{1 - \left(\frac{\delta}{xc}\right)^2} \right] \end{aligned} \quad (27a)$$

Similarly, on combining equations 5, 24, and 26, we obtain for the apparent acidic dissociation constant the expression

$$K_a = \frac{(xc + \delta)\delta}{(xc - \delta)} \quad (28)$$

from which it is evident that

$$K_a > \delta \quad (29)$$

Since for a salt of a simple base, such as ammonium hydroxide or aniline, the ratio

$$\frac{K_b}{K_w} = \frac{1 - x}{x^2c} \quad (30)$$

it is obvious that the quantity  $1/[1 - (\delta/xc)^2]$  in equation 27a can be regarded as a correction factor. The correction will be *increased* if we substitute  $K_a$  for  $\delta$  in this factor. We may write, therefore,

$$\frac{K_b}{K_w} = \frac{1 - x}{x^2c} \left[ \frac{1}{1 - \left(\frac{K_a}{xc}\right)^2} \right] \quad (31)$$

Now, if it can be shown that the correction factor

$$1 - \left( \frac{K_a}{xc} \right)^2$$

is negligible, the true correction will be still more negligible. It is evident from the values given in Table CIX that when  $K_b < 10^{-9}$  (i.e., when the determination of the basic dissociation is possible by means of hydrolysis measurements) we have, at the dilutions usually employed ( $V < 100$ ),  $xc > 10^{-4}$ . If, therefore,  $K_a$  is less than  $10^{-5}$ , the correction will be less than 1 per cent. Table CXXIII, which was prepared

TABLE CXXIII

Value of the constant that is to be determined by measurement of the hydrolysis of a salt	Allowed limits for the other constant. The constant must not exceed the value:		The degree of hydrolysis of the salt has the value:	
	At $c = 0.1$	At $c = 0.01$	At $c = 0.1$	At $c = 0.01$
$10^{-9}$	$5 \times 10^{-6}$	$1.5 \times 10^{-6}$	0.010	0.031
$10^{-10}$	$1 \times 10^{-5}$	$4 \times 10^{-6}$	0.031	0.096
$10^{-11}$	$4 \times 10^{-5}$	$1 \times 10^{-5}$	0.096	0.270
$10^{-12}$	$1 \times 10^{-4}$	$1.5 \times 10^{-5}$	0.270	0.618
$10^{-13}$	$1.5 \times 10^{-4}$	$7 \times 10^{-5}$	0.618	0.916

by Lundén,<sup>1</sup> gives the limiting value that the dissociation constant which is neglected can have if the error in  $K_b/K_w$  (or  $K_a$ ) is to be less than 1 per cent, when the simple equation 30 is employed instead of the true one, 27a.

Evidently, the smaller dissociation constant of an ampholyte may be calculated from the results of hydrolysis measurements, in exactly the same way as for simple acids and bases, provided that the other constant is not too large. When the other constant exceeds the limiting value given in Table CXXIII, equation 30 is not applicable and the correction must be introduced. The methods employed for the determination of the degree of hydrolysis of a salt have been described in Chapter XIX.

In Table CXXIV are given values of the apparent acidic and basic dissociation constants of a number of ampholytes at 25°.

<sup>1</sup> *J. Biol. Chem.*, **4**, 267 (1908).

TABLE CXXIV

DISSOCIATION CONSTANTS OF AMPHOLYTES

Ampholyte	$K_a$	$K_b$
Dimethylpyrnone	$0.8 \times 10^{-14}$	$2 \times 10^{-14}$
Acetoxime	$6.0 \times 10^{-13}$	$6.5 \times 10^{-13}$
Methylglycine	$1.2 \times 10^{-10}$	$1.7 \times 10^{-12}$
Dimethylglycine	$1.3 \times 10^{-10}$	$9.8 \times 10^{-13}$
Leucine	$1.8 \times 10^{-10}$	$2.3 \times 10^{-12}$
Glycine	$1.8 \times 10^{-10}$	$2.7 \times 10^{-12}$
Asparagine	$1.4 \times 10^{-9}$	$1.5 \times 10^{-12}$
Phenylalanine	$2.5 \times 10^{-9}$	$1.3 \times 10^{-12}$
Leucylglycine	$1.5 \times 10^{-8}$	$3 \times 10^{-11}$
Alanylglycine	$1.8 \times 10^{-8}$	$2 \times 10^{-11}$
Glycylglycine	$1.8 \times 10^{-8}$	$2 \times 10^{-11}$
Cacodylic acid	$6.4 \times 10^{-7}$	$3.6 \times 10^{-13}$
Methyl- <i>o</i> -aminobenzoic acid	$4.6 \times 10^{-6}$	$4.6 \times 10^{-13}$
<i>o</i> -Aminobenzoic acid	$1.06 \times 10^{-5}$	$1.37 \times 10^{-12}$
<i>p</i> -Aminobenzoic acid	$1.21 \times 10^{-5}$	$2.33 \times 10^{-12}$
<i>m</i> -Aminobenzoic acid	$1.63 \times 10^{-5}$	$1.22 \times 10^{-11}$
Aspartic acid	$1.5 \times 10^{-4}$	$1.2 \times 10^{-12}$

**Bjerrum's Theory of Ampholytic Dissociation.** From the values given in Table CXXIV, it will be observed that the acidic and basic dissociation constants of the amino acids are much smaller than those of the ordinary carboxylic acids and amines. This is the opposite of what would be predicted from the dissociation of dibasic acids, in which, as we have seen, the first carboxyl group represses the dissociation of the second group. Accordingly, an increase in dissociation would be expected when a positive group, like  $\text{NH}_2$ , was in juxtaposition to the carboxyl group, as in amino acids.

Bjerrum<sup>1</sup> put forward a theory of ampholytic dissociation in which he assumed that in solutions of amino acids the undissociated acid,  $\text{HXOH}$ , is present in negligible amounts; and that the *Zwitterion*,  $^+\text{X}^-$ , exists in appreciable quantities. In accordance with these assumptions we have, therefore, for the acidic and basic dissociation constants the new expressions

$$k_a = \frac{[^+\text{X}^-][\text{H}^+]}{[\text{HX}^+]} \quad (32)$$

and

$$k_b = \frac{[^+\text{X}^-][\text{OH}^-]}{[\text{XOH}^-]} \quad (33)$$

<sup>1</sup> *Z. physik. Chem.*, **104**, 147 (1923).

If the old apparent dissociation constants  $K_a$  and  $K_b$  are known, the new quantities  $k_a$  and  $k_b$  may be calculated, for  $S$  in the previous representation is identical with  $[^+X^-]$  in the new. From equations 5, 6, 32, and 33, we obtain

$$k_a = \frac{K_w}{K_b} \quad (34)$$

and

$$k_b = \frac{K_w}{K_a} \quad (35)$$

It will be observed that the new dissociation constant,  $k_a$ , is identical with the hydrolytic constant corresponding to the old apparent basic dissociation constant; and that  $k_b$  is equal to the hydrolytic constant corresponding to the old apparent acidic dissociation constant. Values of  $k_a$  and  $k_b$  for a number of amino acids at  $25^\circ$ , that have been calculated by Bjerrum by means of equations 34 and 35, are given in Table CXXV.

TABLE CXXV

BJJERRUM'S VALUES OF THE DISSOCIATION CONSTANTS OF AMINO ACIDS

Amino Acid	$k_a$	$k_b$
Betaine	$10^{-1.34}$	ca. 1
Dimethylglycine	$10^{-1.93}$	$10^{-4.05}$
Lysine	$10^{-1.94}$	$10^{-1.9}$
Phenylalanine	$10^{-2.01}$	$10^{-5.30}$
<i>o</i> -Aminobenzoic acid	$10^{-2.04}$	$10^{-8.92}$
Asparagine	$10^{-2.08}$	$10^{-5.03}$
Methylglycine	$10^{-2.15}$	$10^{-4.01}$
Glycine	$10^{-2.33}$	$10^{-4.15}$
Glycylglycine	$10^{-3.20}$	$10^{-6.16}$
Leucylglycine	$10^{-3.38}$	$10^{-6.08}$

It will be observed that these values are larger than those of the dissociation constants of the ordinary carboxylic acids and amines. Moreover, the new values are in agreement with the constitution of the amino acids. Thus, the amino group in asparagine, which contains two carboxyl groups, and the carboxyl group in lysine, which contains two amino groups, would be expected to dissociate to a large extent. The new value of  $k_b$  of the former ampholyte and that of  $k_a$  of the latter are in harmony with these predictions.

## PROBLEMS

1. The apparent basic dissociation constant of a certain ampholyte is  $10^{-12}$  and the acidic constant is  $10^{-6}$ , at  $25^{\circ}$ . Given that the ionic product of water is  $1.2 \times 10^{-14}$  at  $25^{\circ}$ , calculate the concentrations of the two cations of the ampholyte at dilutions of 1, 10, and 100 liters.

2. From the data obtained in the preceding problem, calculate the apparent dissociation constant of the ampholyte for the same dilutions.

3. At  $25^{\circ}$ , the equivalent conductance of *p*-aminobenzoic acid is 7.53 at a dilution of 64 liters, and 355 at infinite dilution. From these data, calculate (a) the concentrations of the two cations of the ampholyte, and (b) the apparent acidic dissociation constant, being given that the degree of hydrolysis of the chloride of the acid is 0.4919 in 0.01 normal solution, and that the ionic product of water is  $1.2 \times 10^{-14}$ .

## CHAPTER XXIII

### HETEROGENEOUS EQUILIBRIA

In the electrolytic equilibria dealt with so far, we have considered only homogeneous systems. We shall now discuss briefly one other important type of equilibria, namely, that which occurs when a solid electrolyte is in contact with its saturated solution. Such equilibria, in which the concentration of the electrolyte is limited by its solubility, are of fundamental importance in analytical chemistry.

**The Solubility Product.** Let us consider a slightly soluble binary electrolyte, MA. On shaking this up with water, a saturated solution is obtained. The salt which goes into solution will be dissociated, the ions being in equilibrium with the solid:



In accordance with the law of mass action, the equilibrium between the solid salt and its ions is governed by the equation

$$\frac{[\text{M}^+][\text{A}^-]}{\left[ \underset{\text{(solid)}}{\text{MA}} \right]} = K \quad (2)$$

Since the quantity in the denominator of equation 2 is constant, we may write

$$[\text{M}^+][\text{A}^-] = \text{Const.} \times K = L \quad (3)$$

The constant  $L$ , which is called the **solubility product** or the **ionic product** of the electrolyte, is equal to the product of the concentrations of its ions in a *saturated* solution. The relation expressed by the solubility product was first derived by Nernst.<sup>1</sup> Although the validity of the theoretical derivation of this relation is open to question,<sup>2</sup> it has been found experimentally that, in dilute solutions, the relation satisfies all but the most rigorous requirements.

Where we are dealing with a very sparingly soluble substance, such as silver chloride, the concentration of either the cation or the anion is

<sup>1</sup> *Z. physik. Chem.*, **4**, 372 (1889).

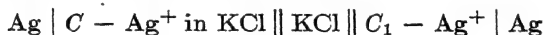
<sup>2</sup> Cf. Stieglitz, *J. Am. Chem. Soc.*, **30**, 946 (1908).

identical with the solubility ( $S$ ) of the electrolyte. Accordingly, for a binary electrolyte,

$$[M^+] = [A^-] = \sqrt{L} = S \quad (4)$$

That is, the solubility of a sparingly soluble binary electrolyte, when alone in the solvent, is equal to the square root of its solubility product. If, then, either the solubility in pure solution or the solubility product is known, the other quantity may be calculated. The solubility product, and therefore the solubility, of sparingly soluble salts may be determined readily by means of electromotive-force measurements.

Suppose, for example, that we wish to determine the solubility of silver chloride. A saturated solution of this salt is prepared by adding, drop by drop, a dilute solution of silver nitrate to a dilute solution of potassium chloride of known ionic concentration ( $C_2$ ), until a precipitate forms. This saturated solution of silver chloride is combined in a concentration cell, constructed according to the scheme:



The electromotive force of the cell is then measured, and the concentration,  $C$ , of the silver ions in the potassium chloride solution is calculated by means of equation 2, Chapter IX. Since the solubility product of silver chloride is equal to the product of the concentrations of the silver and chlorine ions, we have

$$S = \quad (5)$$

**The Influence of the Presence of a Mutual Ion on the Solubility of an Electrolyte.** Let us now consider the effect of adding, to a saturated solution of an electrolyte MA, a second electrolyte M'A, with a mutual ion. This addition increases the concentration of the  $A^-$  ions, and, therefore, the product  $[M^+][A^-]$  will exceed the value of the solubility product,  $L_{MA}$ . Since, however, the solubility product remains constant, the ions  $M^+$  and  $A^-$  must unite to form solid MA, until their concentrations are reduced to such an extent that  $[M^+][A^-] = L_{MA}$ . In other words, the addition of an electrolyte to a saturated solution of another electrolyte with a mutual ion decreases the solubility of the latter. If the electrolyte MA is but slightly soluble, the reduction in the concentration of the ion  $M^+$ , which occurs on the addition of the electrolyte M'A, may be taken as equal to the reduction in the solubility of MA.

From what has been said, it should be evident that the solubility of MA must also be decreased by the addition of an electrolyte MA'; and that the solubility of MA must be decreased to the same extent by equimolar additions of either M'A or MA'. This conclusion, which is



known as the Nernst solubility law, has been tested experimentally by Noyes,<sup>1</sup> Goodwin,<sup>2</sup> Creighton and Ward,<sup>3</sup> and others. The agreement between their results and the theoretical is sufficiently close to substantiate the law of solubility influence. Table CXXVI, which contains the results of Creighton and Ward's measurements at 25°, illustrates the influence of equimolar additions of potassium nitrite or silver nitrate upon the solubility of silver nitrite.

TABLE CXXVI

CHANGES IN SOLUBILITY DUE TO PRESENCE OF MUTUAL ION

Concentration of AgNO <sub>3</sub> or KNO <sub>2</sub> in Moles per Liter	Solubility of Silver Nitrite in the Presence of		
	Silver Nitrate		Potassium Nitrite
	Moles per 1000 cc of Solution		Moles per 1000 cc of Solution
	Observed	Calculated	Observed
0.0000	0.0269	.....	0.0269
0.00258	0.0260	0.0259	0.0259
0.00588	0.0244	0.0247	0.0249
0.01177	0.0224	0.0227	0.0232
0.02355	0.0192	0.0187	0.0203

**Constancy of the Solubility-Product Law.** According to theory, the value of the solubility product of an electrolyte should be independent of the concentration of the added electrolyte. That this is not strictly true is shown by the results of the investigations of Hill and Simmons,<sup>4</sup> Hill,<sup>5</sup> Bray and Winninghof,<sup>6</sup> Kendall,<sup>7</sup> and others. It has been found that the solubility-product law becomes more and more nearly true, the less soluble the electrolyte and the more dilute the solution. For

<sup>1</sup> *Z. physik. Chem.*, **6**, 241 (1890).

<sup>2</sup> *Ibid.*, **13**, 588 (1894).

<sup>3</sup> *J. Am. Chem. Soc.*, **37**, 2333 (1915).

<sup>4</sup> *Ibid.*, **31**, 821 (1909).

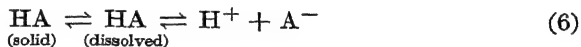
<sup>5</sup> *Ibid.*, **32**, 1186 (1910).

<sup>6</sup> *Ibid.*, **33**, 1674 (1911).

<sup>7</sup> *Proc. Roy. Soc.*, **A85**, 200 (1911).

most purposes, however, the solubility product may be regarded as constant when the solubility of the salt and the concentrations of the ions in the solution are small. Although the value of the solubility product should remain constant in any saturated solution with respect to a given electrolyte, Bray has found that it increases slightly as the total concentration of the salts and ions in the saturated solution increases.

In a saturated solution of a weak electrolyte, e.g., a weak acid, the undissociated molecules are in equilibrium with both the ions and the solid electrolyte:



Since in such a solution the concentration of the undissociated molecules remains constant,

$$[\text{H}^+][\text{A}^-] = \text{Const.} \times K = L \quad (7)$$

With the object of testing the constancy of the solubility-product law, Kendall measured the solubility of a number of slightly soluble acids in aqueous solutions of a second acid. The results of his investigation show that the solubility of an acid in an aqueous solution of another may be regarded as consisting of two parts, one of which (a) increases or decreases regularly according as the acid is more or less soluble in the second acid than in water, while the other (b) decreases more or less rapidly according to the ionic concentration of the second acid. The divergencies between the experimental solubility values and those required by the theory of the constant solubility product can always be accounted for by the solvent effect (a). According to whether the acids are chemically similar (e.g., salicylic and *ortho*-nitrobenzoic acid) or dissimilar (e.g., hydrochloric and salicylic acid), the divergencies are positive or negative.

It should be remembered that, as Arrhenius<sup>1</sup> pointed out, the inconsistency of the solubility product under certain conditions may be due to the fact that the solvent medium is somewhat changed by the presence of the other electrolyte.

**Calculation of the Solubility of an Electrolyte in the Presence of Another with a Mutual Ion.** The influence of a second electrolyte upon the solubility of another with a mutual ion is governed by these laws: (1) In a saturated solution of a partially dissociated electrolyte, the concentration of the undissociated portion remains constant even when another dissociated substance is added; (2) the product of the concentrations of the ions of an electrolyte remains constant even when another electrolyte

<sup>1</sup> *Z. physik. Chem.*, **31**, 197 (1899).

with a mutual ion is added. These two laws may be expressed as follows:

$$S_0(1 - \alpha_0) = S(1 - \alpha) \quad (8)$$

$$(S_0\alpha_0)^2 = S\alpha(S\alpha + c\alpha_1) \quad (9)$$

where  $S_0$  and  $S$  represent the solubility of the first electrolyte before and after the addition of the second,  $\alpha_0$  and  $\alpha$  the degree of dissociation of the first electrolyte before and after the addition of the second, and  $\alpha_1$  the degree of dissociation and  $c$  the concentration of the second electrolyte in the mixture. In the foregoing equations,  $S_0$ ,  $S$ , and  $c$  are expressed in moles per liter. On solving these equations, we find that the solubility of an electrolyte in the presence of a second with a mutual ion is given by either

$$S = -\frac{c\alpha_1}{2\alpha} + \sqrt{S_0^2 \frac{\alpha_0^2}{\alpha^2} + \frac{c^2}{4} \left(\frac{\alpha_1}{\alpha}\right)^2} \quad (10)$$

or

$$S = S_0 \frac{1 - \alpha_0}{1 - \alpha} \quad (11)$$

Theoretically, these two equations are identical. Although the second equation is the simpler, it is obviously inapplicable to strong (completely dissociated) electrolytes, or when the degree of dissociation ( $\alpha$ ) is large, for the value of  $S$  would be greatly influenced by small errors in  $\alpha$ . Equation 10 was employed by Noyes, Creighton and Ward (see Table CXXVI, column 3), and others to calculate the solubility of an electrolyte in the presence of different concentrations of another with a mutual ion.

**The Formation of Double and Complex Salts.** Sometimes the addition of the electrolyte  $M'A$  is found to cause either an immediate increase in the solubility of  $MA$ , or a decrease followed by an increase. Such behavior is not due to a breakdown of the solubility-product law but, as Hoitsema<sup>1</sup> showed, to reactions which occur between the two electrolytes, double salts,  $MA \cdot M'A$  or  $MM'A_2$ , or complex salts  $M(M'A_2)$ , being formed. When the electrolytes react to form double salts, although the first additions of  $M'A$  decrease the solubility of  $MA$ , the solubility may reach a minimum and then increase as the formation of the double salt increases. If complex salts are formed by the electrolytes, the effects are different. Here, on the addition of  $M'A$ , the  $A^-$  ions, say, of

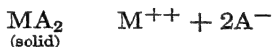
<sup>1</sup> *Z. physik. Chem.*, **24**, 577 (1897).

the first electrolyte are consumed in the formation of the complex ion  $(M'A_2)^-$ . Since, however, the solubility product

$$L_{MA} = [M^+][A^-]$$

must remain constant, new  $A^-$  ions are formed from the solid MA, thus increasing the solubility of this electrolyte. Continued addition of  $M'A$  increases the solubility of MA, until the solution becomes saturated with the complex salt  $M(M'A_2)$ .<sup>1</sup>

**Ternary Electrolytes.** The lowering of the solubility of a ternary electrolyte by an electrolyte containing a mutual ion was calculated by Noyes.<sup>2</sup> For a slightly soluble ternary electrolyte,  $MA_2$ , which dissolves in accordance with the equation



the solubility product is given by

$$L = [M^{++}][A^-]^2 \quad (12)$$

A general discussion of the solubility relations involved in solutions of salts of higher types may be found in papers by Noyes, Bray, Harkins, and Winninghof.<sup>3</sup>

**The Formation and Conversion of Precipitates.** We shall now consider what occurs on bringing together two aqueous solutions, each of which contains an ion of a slightly soluble substance—for example, solutions containing silver nitrate and sodium chloride. In accordance with the solubility-product law, equilibrium can exist between the silver and chlorine ions only when

$$[Ag^+][Cl^-] = L_{AgCl}$$

Therefore, whether silver chloride precipitates from the solution depends upon whether the product of the concentrations of the silver and chlorine ions in the mixture exceeds the value of the solubility product of silver chloride, for precipitation occurs only when

$$[Ag^+][Cl^-] > L_{AgCl}$$

If equivalent quantities of sodium chloride and silver nitrate are brought together in solution, silver chloride will precipitate until the concentrations of the silver and chlorine ions are reduced to such an extent that

$$[Ag^+][Cl^-] = L_{AgCl}$$

<sup>1</sup> In this connection see Harkins and Paine, *J. Am. Chem. Soc.*, **41**, 1155 (1919).

<sup>2</sup> *Z. physik. Chem.*, **9**, 603 (1892).

<sup>3</sup> *J. Am. Chem. Soc.*, **33**, 1643, 1663, 1673, 1807, 1827, 1836 (1911).

Since the value of the solubility product of silver chloride is extremely small ( $1.56 \times 10^{-10}$ ), the quantity of silver chloride that remains in solution is very small. If an excess of either sodium chloride or silver nitrate is now added to the solution, it is obvious that the product of the concentrations of the silver and chlorine ions will exceed the value of the solubility product of silver chloride and, in consequence, a further precipitation of silver chloride will result. It is for this reason that an excess of the precipitating reagent is used in analysis. This is most essential in precipitating a substance with a relatively high solubility product, such as lead chloride ( $L = 1 \times 10^{-4}$ ), as is illustrated by the following data:

SOLUBILITY OF LEAD CHLORIDE

Temperature	20°	80°
In water	1.18	3.1
In 10% HCl	0.14	1.2

A knowledge of the value of the solubility product is of fundamental importance in the formation and conversion of precipitates, as Findlay<sup>1</sup> pointed out.

The dissolution of a precipitate depends upon the fact that one of its ions unites with one of the ions of the added substance. Since this decreases the product of the ion-concentrations below the value of the solubility product of the precipitate, some of the precipitate must dissolve. This process may continue until all the precipitate has been dissolved. It is for this reason that the sparingly soluble compounds containing the anions of hydrogen sulphide, carbonic acid, phosphoric acid, hydrocyanic acid, oxalic acid, and the hydroxides are dissolved by acids.

If solid silver chloride is treated with a solution of potassium bromide, how much silver bromide will be formed? Evidently, this will depend upon the concentration of the potassium bromide, and upon the ratio of the solubility products of the two silver salts. The equilibrium between the silver and chlorine ions is given by the expression

$$[\text{Ag}^+][\text{Cl}^-] = L_{\text{AgCl}} = 1.56 \times 10^{-10}$$

and that between the silver and bromine ions by the expression

$$[\text{Ag}^+][\text{Br}^-] = L_{\text{AgBr}} = 4.35 \times 10^{-13}$$

Therefore,

$$\frac{L_{\text{AgCl}}}{L_{\text{AgBr}}} = \frac{[\text{Cl}^-]}{[\text{Br}^-]} = 358.6$$

<sup>1</sup> *Z. physik. Chem.*, **34**, 413 (1900).

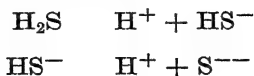
Hence, chlorine ions must go into solution and bromine ions precipitate out, until the concentrations of these ions are such that their ratio is equal to 358.6. On the other hand, silver bromide will dissolve in a solution of potassium chloride, but to a very limited extent.

A practical application of the conversion of precipitates was made by Lord Kelvin in his instrument for deep-sea sounding. This consists of a long glass tube, encased in brass and open at the lower end, which is coated on the inside with silver chromate ( $L = 1 \times 10^{-11}$ ). When this tube is lowered into the ocean, the water rises inside and the high concentration of the chlorine ions in the water converts the brown silver chromate into white silver chloride. Since the maximum height to which the water rises inside the tube is indicated by the white-brown junction on the walls, the compression of the air inside and, therefore, the maximum depth to which the tube sinks can be calculated.

Many of the results obtained in analytical chemistry are readily explained by means of the solubility-product law. Thus, although both copper and cadmium are precipitated by potassium ferrocyanide, practically all the copper can be precipitated from a solution containing the two metals before any of the cadmium comes down, owing to the fact that the solubility product of copper ferrocyanide is much smaller than that of cadmium ferrocyanide. The success of Mohr's volumetric method for the determination of the chlorine in a soluble chloride by titration with silver nitrate, in the presence of potassium chromate, depends upon the marked difference in the solubilities of silver chromate and silver chloride. In qualitative analysis, calcium, for example, may be precipitated along with the metals of the iron and aluminum groups, when the phosphate ion is present. In order to recover the calcium (and other alkaline-earth metals), the phosphate ion must be removed from solution. This may be accomplished by adding ferric chloride and ammonium acetate to the slightly acid solution containing the calcium and the metals of the iron group. The ammonium acetate reduces the hydrogen-ion concentration of the solution to a small value, and practically all the phosphate ion precipitates as ferric phosphate. That none of the calcium precipitates as phosphate is due to the fact that the solubility product of ferric phosphate is very much smaller than that of calcium phosphate.

**The Solubility of the Metallic Sulphides.** The most insoluble substances are to be found among the sulphides. Since the whole of our analytical procedure for the detection of the metals is based upon the insolubility of their sulphides, it is important that we discuss the precipitation of the sulphides in some detail.

The dissociation of hydrogen sulphide, like that of other ternary electrolytes, takes place in two stages:



These dissociations are governed by the following equations:

$$\frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]} = K_1 \quad (13)$$

$$\frac{[\text{H}^+][\text{S}^{--}]}{[\text{HS}^-]} = K_2 \quad (14)$$

from which it follows that

$$\frac{[\text{H}^+]^2[\text{S}^{--}]}{[\text{H}_2\text{S}]} = K_1 K_2 = K \quad (15)$$

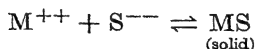
It was found by Auerbach<sup>1</sup> that the first dissociation constant,  $K_1$ , of hydrogen sulphide is equal to  $0.91 \times 10^{-7}$  at  $18^\circ$ , and by Knox<sup>2</sup> that the second dissociation constant,  $K_2$ , is equal to  $1.2 \times 10^{-15}$  at  $25^\circ$ . The dissociation constant  $K$  of hydrogen sulphide, then, is approximately equal to  $10^{-22}$  at room temperature.

It is evident, from the very small value of the dissociation constant of hydrogen sulphide, that even in a saturated solution of the gas the concentration of the sulphur ions is extremely small. This concentration is very much smaller still in the presence of a strong acid like hydrochloric or nitric acid. Accordingly only the most insoluble sulphides (e.g., those of Ag, Hg, Pb, Bi, Cu, As, Pt, and Au) can be precipitated completely from a strongly acid solution by hydrogen sulphide. In other words, these sulphides are not dissolved by moderately concentrated solutions of strong acids. Since the very insoluble sulphides (e.g., those of Cd, Sb, and Sn) require a somewhat higher, although still small, concentration of sulphur ions for their precipitation, they are not completely precipitated from moderately concentrated solutions of strong acids. The appreciably soluble sulphides (e.g., those of Zn, Co, and Ni) require for their precipitation a sulphur-ion concentration attainable only in neutral solution or in solutions of a weak acid. The markedly soluble sulphides (e.g., those of Mn and Fe) require for their precipitation a sulphur-ion concentration found only in alkaline solutions. In other words, these sulphides are dissolved by even the weakest acids.

<sup>1</sup> *Z. physik. Chem.*, **49**, 217 (1904).

<sup>2</sup> *Trans. Faraday Soc.*, **4**, 29 (1908).

In the precipitation of a bivalent metal by hydrogen sulphide the following equilibria must be considered:



for which

$$L_{MS} = [M^{++}][S^{--}]$$

and



for which

$$K_{H_2S} = \frac{[H^+]^2[S^{--}]}{[H_2S]}$$

On combining these equations, we obtain

$$K_{H_2S} = \frac{[H^+]^2 L_{MS}}{[H_2S][M^{++}]}$$

whence, since  $K_{H_2S}$  and  $L_{MS}$  are constant,

$$[M^{++}] = K_1 \frac{[H^+]^2}{[H_2S]} \quad (16)$$

Equation 16 shows that the concentration of the metal remaining in solution when equilibrium is reached is directly proportional to the square of the concentration of the hydrogen ions and inversely proportional to the concentration of the hydrogen sulphide in the solution. For univalent and trivalent metals we have, respectively,

$$[M^+] = \sqrt{\frac{K_2[H^+]^2}{[H_2S]}} \quad (17)$$

and

$$[M^{+++}] = \sqrt{\frac{K_3[H^+]^6}{[H_2S]^3}} \quad (18)$$

(Let the student derive equations 17 and 18.)

**Numerical Values of Solubility Products.** On account of the important part played in analytical chemistry by precipitation reactions and, therefore, by heterogeneous equilibria, the numerical values of the solubility products of a number of difficultly soluble substances are given in Table CXXVII. The values in this table have been taken from the papers of Noyes,<sup>1</sup> Kohlrausch and Rose,<sup>2</sup> Goodwin,<sup>3</sup> Morgan,<sup>4</sup>

<sup>1</sup> *Z. physik. Chem.*, **6**, 241 (1890).

<sup>3</sup> *Ibid.*, **13**, 641 (1894).

<sup>2</sup> *Ibid.*, **12**, 234 (1893).

<sup>4</sup> *Ibid.*, **17**, 533 (1895).



TABLE CXXVII  
 NUMERICAL VALUES OF SOLUBILITY PRODUCTS

Substance	Formula	Temperature, °C	Solubility Product
Silver nitrite	AgNO <sub>2</sub>	25	$5.86 \times 10^{-4}$
Silver bromate	AgBrO <sub>3</sub>	24.5	$6.6 \times 10^{-6}$
Silver iodate	AgIO <sub>3</sub>	25	$3.6 \times 10^{-8}$
Silver chloride	AgCl	25	$1.56 \times 10^{-10}$
Silver oxalate	Ag <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	25	$1.3 \times 10^{-11}$
Silver chromate	Ag <sub>2</sub> CrO <sub>4</sub>	18	$1.0 \times 10^{-11}$
Silver thiocyanate	AgSCN	25	$2.56 \times 10^{-12}$
Silver bromide	AgBr	25	$4.35 \times 10^{-13}$
Silver cyanide	AgCN	17.5	$1.0 \times 10^{-13}$
Silver iodide	AgI	25	$9.4 \times 10^{-17}$
Silver sulphide	Ag <sub>2</sub> S	18	$6.4 \times 10^{-32}$
Mercurous chloride	Hg <sub>2</sub> Cl <sub>2</sub>	25	$3.5 \times 10^{-18}$
Mercurous bromide	Hg <sub>2</sub> Br <sub>2</sub>	25	$1.3 \times 10^{-21}$
Mercurous iodide	Hg <sub>2</sub> I <sub>2</sub>	25	$1.2 \times 10^{-28}$
Mercuric chloride	HgCl <sub>2</sub>	25	$2.6 \times 10^{-15}$
Mercuric bromide	HgBr <sub>2</sub>	25	$8 \times 10^{-20}$
Mercuric iodide	HgI <sub>2</sub>	25	$3.2 \times 10^{-29}$
Lead chloride	PbCl <sub>2</sub>	25.2	$1.0 \times 10^{-4}$
Lead bromide	PbBr <sub>2</sub>	25.2	$6.0 \times 10^{-6}$
Lead iodide	PbI <sub>2</sub>	25.2	$1.0 \times 10^{-7}$
Lead sulphate	PbSO <sub>4</sub>	25.2	$2.2 \times 10^{-8}$
Lead sulphide	PbS	....	$10^{-50}$
Cuprous chloride	Cu <sub>2</sub> Cl <sub>2</sub>	....	$1.2 \times 10^{-6}$
Cuprous bromide	Cu <sub>2</sub> Br <sub>2</sub>	....	$4.15 \times 10^{-8}$
Cuprous iodide	Cu <sub>2</sub> I <sub>2</sub>	....	$5.06 \times 10^{-12}$
Cuprous sulphide	Cu <sub>2</sub> S	....	$2 \times 10^{-47}$
Cupric sulphide	CuS	....	$3 \times 10^{-42}$
Thallous sulphate	Tl <sub>2</sub> SO <sub>4</sub>	25	$3.6 \times 10^{-4}$
Thallous chloride	TlCl	25	$2.65 \times 10^{-4}$
Thallous thiocyanate	TlSCN	25	$2.25 \times 10^{-4}$
Thallous bromide	TlBr	25	$4 \times 10^{-6}$
Magnesium carbonate	MgCO <sub>3</sub>	12	$1.93 \times 10^{-4}$
Magnesium hydroxide	Mg(OH) <sub>2</sub>	....	$1.22 \times 10^{-11}$
Calcium sulphate	CaSO <sub>4</sub>	....	$6.11 \times 10^{-5}$
Calcium carbonate	CaCO <sub>3</sub>	16	$0.98 \times 10^{-8}$
Calcium oxalate	CaC <sub>2</sub> O <sub>4</sub>	18	$0.84 \times 10^{-8}$
Strontium sulphate	SrSO <sub>4</sub>	18	$1.3 \times 10^{-6}$
Strontium oxalate	SrC <sub>2</sub> O <sub>4</sub>	18	$2.6 \times 10^{-7}$
Strontium carbonate	SrCO <sub>3</sub>	18	$2.3 \times 10^{-8}$
Barium oxalate	BaC <sub>2</sub> O <sub>4</sub>	18	$4.3 \times 10^{-7}$
Barium carbonate	BaCO <sub>3</sub>	18	$0.7 \times 10^{-8}$
Barium chromate	BaCrO <sub>4</sub>	18	$\times 10^{-10}$
Barium sulphate	BaSO <sub>4</sub>	18	$5.3 \times 10^{-10}$

Bernfeld,<sup>1</sup> von Ende,<sup>2</sup> Immerwald,<sup>3</sup> Bodlander,<sup>4</sup> Sherrill,<sup>5</sup> Abegg and Cox,<sup>6</sup> Johnston,<sup>7</sup> Creighton and Ward,<sup>8</sup> Trümpler,<sup>9</sup> and Jellinek and Czerwinski.<sup>10</sup> In Table CXXVIII are given values of the solubility products of a number of metallic sulphides which have been calculated<sup>11</sup> from the free energies of formation of the crystalline compounds.

TABLE CXXVIII

NUMERICAL VALUES OF SOLUBILITY PRODUCTS OF METALLIC SULPHIDES

Sulphide of:	Formula	Solubility Product
Bismuth	$\text{Bi}_2\text{S}_3$	$7.1 \times 10^{-61}$
Antimony	$\text{Sb}_2\text{S}_3$	$2.9 \times 10^{-59}$
Silver	$\text{Ag}_2\text{S}$	$5.9 \times 10^{-52}$
Copper (ous)	$\text{Cu}_2\text{S}$	$2.6 \times 10^{-49}$
Copper (ic)	$\text{CuS}$	$3.2 \times 10^{-38}$
Lead	$\text{PbS}$	$6.8 \times 10^{-29}$
Cadmium	$\text{CdS}$	$1.2 \times 10^{-28}$
Tin	$\text{SnS}$	$1.0 \times 10^{-27}$
Zinc	$\text{ZnS}$	$7.4 \times 10^{-27}$
Cobalt ( $\alpha$ )	$\text{CoS}$	$3.1 \times 10^{-23}$
Iron	$\text{FeS}$	$3.8 \times 10^{-20}$
Manganese	$\text{MnS}$	$1.1 \times 10^{-15}$
Magnesium	$\text{MgS}$	$2.0 \times 10^{-15}$

## PROBLEMS

1. Explain why it is necessary, in the Volhard method for the estimation of the chlorine in chlorides, to filter off the precipitated silver chloride before determining the excess of silver with potassium thiocyanate.

2. The specific conductance of a saturated solution of silver chloride at  $18^\circ$  is  $1.397 \times 10^{-6}$  mho. On the assumption that the silver chloride is completely dissociated, calculate its solubility and solubility product, given that the equivalent conductances of potassium chloride, potassium nitrate, and silver nitrate at zero concentration are 130.1, 126.6, and 115.8, respectively.

<sup>1</sup> *Ibid.*, **25**, 72 (1898).

<sup>2</sup> *Z. anorg. Chem.*, **26**, 129 (1901).

<sup>3</sup> *Z. Elektrochem.*, **7**, 477 (1901).

<sup>4</sup> *Z. anorg. Chem.*, **31**, 458 (1902).

<sup>5</sup> *Z. physik. Chem.*, **43**, 705 (1903).

<sup>6</sup> *Ibid.*, **46**, 1 (1903).

<sup>7</sup> *J. Am. Chem. Soc.*, **37**, 2001 (1915).

<sup>8</sup> *Ibid.*, **37**, 2333 (1915).

<sup>9</sup> *Z. physik. Chem.*, **99**, 9 (1921).

<sup>10</sup> *Ibid.*, **102**, 438 (1922).

<sup>11</sup> Kapustinokiĭ, *Compt. rend. acad. sci. U.R.S.S.*, **28**, 144 (1940) (in English).

3. The solubilities of silver bromide and silver iodide at  $25^\circ$  are  $6.6 \times 10^{-7}$  and  $9.7 \times 10^{-9}$  mole per liter, respectively. If 5 grams of silver bromide is treated with 100 cc of a 0.2 normal solution of potassium iodide, what weight of silver bromide will be transformed into silver iodide?

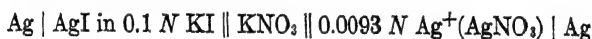
4. A solution of potassium thiocyanate, containing 0.505 mole per liter, was shaken with an excess of silver chloride at  $25^\circ$ . After equilibrium was established, it was found that the solution contained 0.500 mole of potassium chloride per liter. Assuming that the potassium and silver salts are completely dissociated, calculate the solubility product of silver chloride, given that the solubility product of silver thiocyanate is  $10^{-12}$ .

5. It has been found that  $\alpha$ -bromisocinnamic acid is 58.3 per cent dissociated in a saturated solution at  $25^\circ$ , and that its solubility is 0.0176 mole per liter. When in addition to  $\alpha$ -bromisocinnamic acid the solution contains 0.0272 mole of oxanilic acid per liter, the degree of dissociation of the former acid is 0.453 and that of the latter 0.403. From these data, calculate the solubility of  $\alpha$ -bromisocinnamic acid in 0.0272 molar oxanilic acid.

6. In a saturated aqueous solution the degree of dissociation of silver bromate is 0.949 at  $24.5^\circ$ , and its solubility is 0.00810 mole per liter at the same temperature. Calculate the solubility of the salt in 0.00850 molar silver nitrate.

7. The ratio of the solubilities of the sulphides of two bivalent metals is 1 : 10,000. Calculate the ratio of the hydrogen-ion concentrations at which the metals will be scarcely precipitated by hydrogen sulphide, when each metal has the same concentration.

8. The electromotive force of the cell



is 0.790 volt at  $18^\circ$ . Given that the transference number of the anion in silver nitrate is 0.528, calculate (a) the solubility product and (b) the solubility of silver iodide at  $18^\circ$ .

9. The electromotive force of the cell



is 0.015 volt at  $25^\circ$ . The solubility of silver bromide in pure aqueous solution is  $6.6 \times 10^{-7}$  mole per liter. Neglecting the potential difference at the junction of the two solutions, and assuming that all the salts are completely dissociated, calculate (a) the solubility product and (b) the solubility of silver thiocyanate at  $25^\circ$ .

## CHAPTER XXIV

### THE ELECTROCHEMISTRY OF GASES

So far our attention has been confined solely to the electrochemistry of solutions and fused salts. Before concluding, we shall consider, briefly, the electrochemistry of gases. Although this phase of electrochemistry is complicated by difficulties which do not arise in electrolysis, and although, moreover, there is but little indication at present that it will ever be as fruitful as electrolysis, the importance of the electrochemistry of gases has been recognized, especially in relation to gaseous reactions taking place under the influence of ionization.

**Ionization of Gases. General.** Although in their normal state gases are among the best insulators of electricity, when a very high potential difference is applied to two points within a gas an electrical discharge in the form of a spark takes place between the points. In air at ordinary pressure, a potential difference of several thousand volts is required to produce a spark 1 cm in length. The characteristics of the electrical discharge through a gas vary markedly with its pressure. As the pressure is reduced, the spark broadens out and assumes a brush-like appearance and a bluish color. At a pressure of about 0.5 mm the gas becomes luminous, showing a series of transverse, flickering striae. If the pressure is sufficiently low, rays can be observed proceeding in straight lines from the cathode. These rays, to which the name **cathode rays** has been given, were proved by J. J. Thomson (1895) to consist of negatively charged particles or **electrons**. The mass of the electron is  $9.0 \cdot 10^{-28}$  gram, and its charge  $4.80 \cdot 10^{-10}$  electrostatic unit. As no charge has yet been observed that is smaller than that on the electron, and all other observed charges have been found to be exact integral multiples of the electronic charge, the electron may be regarded as an atom of electricity.

Gases may be rendered partially conducting by the action of certain agents. For example, charged bodies rapidly lose their charge when an X-ray bulb is operated in their vicinity, because the surrounding air becomes temporarily conducting. Conductance may also be conferred on gases by the action of cathode rays, the  $\alpha$ ,  $\beta$ , and  $\gamma$  radiations emitted by radioactive substances, certain chemical reactions, high temperatures, and the action of the photoelectric effect of short-wavelength radiation. These agents are termed **ionizing agents**.

The phenomenon of the conductance of electricity through gases was accounted for by J. J. Thomson and Rutherford on the assumption that the gas is broken up into positively and negatively charged particles, which convey the current across the gas. By analogy with the carriers of electricity in electrolytic conductance, these electrically charged gaseous particles are called **gaseous ions**. In accordance with the current conception of the structure of matter (see p. 48), gaseous ions must consist of atoms or molecules which have gained or lost one or more electrons, or of electrons themselves. The actual existence of gaseous ions was demonstrated experimentally by C. T. R. Wilson and others. By making use of the fact that electrified particles act as nuclei upon which water or other vapor can condense, Wilson succeeded in photographing the path of an ionizing ray in air.

If two parallel plates between which there is a potential difference are placed in a gas which is acted on by an ionizing agent, a current of electricity will flow between the plates. This is due to a movement, under the influence of the electric field between the plates, of the negative ions to the positive plate and the positive ions to the negative plate. If the electric field is weak, many of the ions will recombine before reaching the plate, owing to their mutual attraction, and the current will be small. The strength of the current increases with the strength of the field, until it attains a maximum value—called the **saturation current**—when all the ions formed reach the plates.

The velocity with which an ion moves under the action of the electric field is directly proportional to the strength of the field. For a given gas under given conditions of temperature and pressure, the velocities or the mobilities,  $u$  and  $v$ , of the positive and negative ions, respectively, are:

$$u = k_1 x \quad (1a)$$

$$v = k_2 x \quad (1b)$$

when  $x$  is the strength of the field and  $k_1$  and  $k_2$  are constants. The constant  $k$  is equal to one-half the product of the charge on the ion and the time required for the ion to describe its mean free path, divided by the mass of the ion. In Table CXXIX<sup>1</sup> are given values of  $k_1$  and  $k_2$  for a number of gases at ordinary temperature and pressure.

It will be observed that the mobilities of the ions of a gas decrease as its molecular weight increases; and that the negative ion of the lighter gases has a higher mobility than the positive ion, the difference decreasing as the molecular weight of the gas increases.

<sup>1</sup> Crowther, *Ions, Electrons, and Ionizing Radiations*, p. 27, 1922.

Since the value of the constant  $k$  in equation 1 depends, among other factors, upon the time required by the ion to describe its mean free path, and since, in accordance with the kinetic theory of gases, this path is inversely proportional to the pressure ( $p$ ) of the gas, it follows that the product  $kp$  should be independent of the pressure, provided that the nature of the ion does not change. With a positive ion the value of this product does not change as the pressure of the gas is diminished, indicating that this ion consists of a single charged atom or molecule. With negative ions, on the other hand, the value of  $kp$  rapidly increases as

TABLE CXXIX

RELATIVE MOBILITIES OF GASEOUS IONS

Gas	$k_1$ (+)	$k_2$ (-)
Hydrogen	6.70	7.95
Air	1.36	1.87
Carbon monoxide	1.10	1.14
Carbon dioxide	0.81	0.85
Sulphur dioxide	0.44	0.41
Pentane	0.35	0.35

the pressure of the gas is decreased below about one-tenth of an atmosphere. This shows that the negative ion becomes smaller as the pressure of the gas is reduced; and, since at atmospheric pressure the ion consists of a charged atom or molecule, it is evident that at low pressures the carriers of negative electricity are smaller than an atom or molecule. In other words, at low pressures negative ions, formed by the union of electrons with neutral atoms or molecules, lose electrons. A similar effect on negative ions is brought about by an increase in temperature.

The condensation of water vapor upon gaseous ions may be utilized to determine the electric charge on an ion. The number of drops,  $n$ , in the cloud formed by the condensation is given by the expression

$$\frac{4}{3}\pi r^3 dn = M \quad (2)$$

where  $M$  is the mass of the cloud and  $d$  is the density of water. The radius,  $r$ , of a single drop can be calculated from the speed with which the cloud settles, by means of Stokes' equation (p. 139). Since the quantity of electricity  $Q$ , brought down as the cloud settles under the influence of gravity, can be measured, the charge on a single ion is  $Q/n$ . An ingenious modification of this method, whereby drops formed mechanically by a sprayer in an atmosphere saturated with the liquid

are allowed to acquire charges from the ionized air, was employed by Millikan<sup>1</sup> to determine the value of the unit electric charge. The value obtained is  $4.8024 \cdot 10^{-10}$  electrostatic unit.

**Ionization by Collision.** (a) *The Spark Discharge.* We have seen that the current which flows between two electrodes contained in a gas increases with the strength of the electric field, and ultimately attains a maximum value—the saturation current. Further increase in the

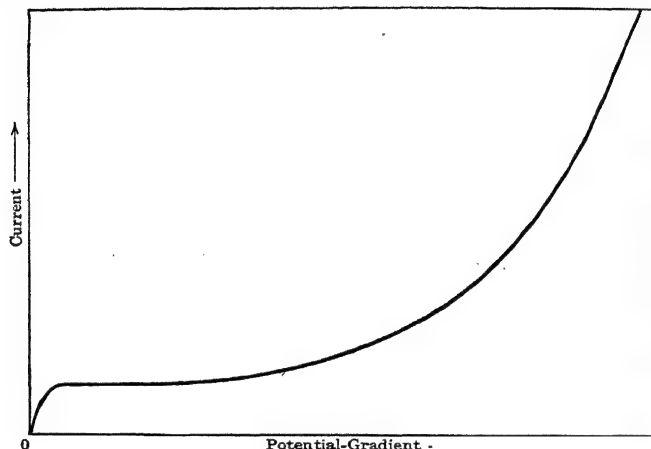


FIG. 86.

strength of the field at first produces no appreciable increase in the current; but if the strength of the field is increased above a definite value the current will begin to increase again, slowly at first and then more rapidly, and finally a spark will pass between the electrodes. The variation in the current with change in the potential gradient between the electrodes is illustrated in Fig. 86. The strength of the field necessary to produce sparking varies with the nature of the gas and increases with the distance between the electrodes and the pressure of the gas.

(b) *The Brush and Dark Discharges.* If the electrodes, one of which is a point, are widely separated, so that the electric field is uniform between them, the electric discharge through the gas gives rise to a luminous brush. This brush, which is formed at that part of the electrode where the field is most intense, consists of a large number of small sparks commencing at the electrode and terminating in the gas. The minimum potential gradient necessary to give rise to a brush discharge depends

<sup>1</sup> *Phys. Rev.*, **39**, 349 (1911); **2**, 143 (1913).

upon the sign of the point electrode, and it is less for a negative than for a positive electrode.

The discharge between a plate and a point electrode frequently begins before any indication of luminosity can be observed. This type of discharge is termed a **dark discharge**. On increasing the *current*, a brush and then a spark discharge take place. Further increase in the current may result in the formation of an arc.

(c) *Ionizing and Resonance Potentials*. The increase in the current through partially ionized gas, above its saturation value, is due to an increased ionization resulting from collisions between electrons and neutral gaseous molecules. The stronger the electric field, the higher is the velocity and, therefore, the energy of the electrons. If this velocity is sufficiently high (of the order of  $10^8$  cm per second), a moving electron will remove completely an outer electron on colliding with a neutral molecule. This will leave the molecule positively charged. The potential through which an electron must fall in order to remove completely an electron from a molecule of a gas is called the **ionizing potential** of the gas. This potential represents the work required to remove an electron from a molecule; but, as Thomson pointed out,<sup>1</sup> since this work must depend upon the way in which it is done, the ionizing potential is not a perfectly definite quantity. Of course, a gas may have several ionizing potentials, corresponding to the removal of 1, 2, 3, etc., outer electrons.

Although the velocity of an electron may not be sufficient to effect the complete removal of an electron from a gaseous molecule, it may be able on collision to *displace* an electron to an orbit further removed from the nucleus. The minimum potential through which an electron must fall in order to cause this displacement is called the **resonance potential** of the gas. Obviously, each kind of atom has many resonance potentials.

The displacement or complete removal of an electron from a gaseous atom or molecule gives rise to spectral lines of definite wavelength which may be employed to calculate the resonance and ionizing potentials ( $E$ ) of a gas, by means of the relation

$$E = \frac{h \cdot c}{e\lambda 10^8} \quad (3)$$

where  $c$  is the velocity of light,  $\lambda$  is the wavelength of the spectral line, and  $h$  is the quantum constant ( $6.624 \times 10^{-27}$  erg per second). In Table CXXX are given the simple ionizing potentials of a number of gases.<sup>2</sup>

<sup>1</sup> *The Electron in Chemistry*, p. 21, 1923.

<sup>2</sup> For experimental methods of measuring resonance and ionizing potentials, the reader is referred to Davis and Goucher, *Phys. Rev.*, **10**, 101 (1917), and Compton, *Phil. Mag.*, **40**, 553 (1920).



TABLE CXXX  
IONIZING POTENTIALS OF GASES \*

Gas	Ionizing Potential Volts	Gas	Ionizing Potential Volts
Caesium	3.877	Zinc	9.353
Rubidium	4.158	Iodine	10.1
Potassium	4.321	Mercury	10.392
Sodium	5.116	Arsenic	11.5
Lithium	5.368	Sulphur	12.2
Barium	5.188	Hydrogen	13.3
Strontium	5.670	Phosphorus	13.3
Calcium	6.087	Argon	15.1
Thallium	7.3	Oxygen	15.5
Magnesium	7.613	Nitrogen	16.9
Cadmium	8.955	Helium	25.6

\* Foote and Mohler, *The Origin of Spectra*, 1922.

For the elements of the first two groups of the periodic table, the change in the value of the simple ionizing potential with atomic weight is approximately what would be expected. The most electronegative elements have the lowest ionizing potentials.

In the Cottrell precipitator there are two parallel electrodes: the one the discharge electrode, and the other the collecting electrode. The potential between the electrodes ranges between 50,000 and 100,000 volts direct current. The dust particles become charged and are attracted to the positive electrode, or the dust or mist particles may be carried along more or less mechanically in the path of the high-potential or corona discharge. From time to time, the collecting electrodes are agitated and the dust collected in suitable receptacles at the bottom of the electrode.<sup>1</sup>

**Ionization by Rays.** It has been pointed out already that gases may be ionized by the action of radiations such as ultraviolet light, X-rays, and the  $\gamma$  rays (identical with X-rays) from radioactive substances. Light of sufficiently short wavelength is able to ionize some gases to a slight extent. For example, the maximum effective wavelength for air is approximately 1350 Å, and for various gaseous compounds, such as ammonia and carbon dioxide, over 1450 Å (i.e., these compounds are ionized by the light transmitted by a thin quartz window). On the other hand, up to the present, failure has attended all attempts to ionize chlorine by light. The degree to which a gas is ionized by X-rays

<sup>1</sup> For a fuller account of the Cottrell precipitator, see Koehler, Vol. II.

depends upon the pressure and the nature of the gas, and to a smaller extent upon the quality of the rays. Under the same conditions the relative ionization of hydrogen, air, and mercury methyl is 1, 100, and 42,500. However, even under the most favorable conditions, the proportion of molecules ionized by X-rays does not exceed 1 in  $10^{12}$ .

**Ionization by Hot Bodies.** (a) *Thermionic Discharge.* It has long been known that hot bodies are unable to retain an electric charge. This is due to the fact that at sufficiently high temperatures hot bodies give off both negative and positive ions to the air. Although these carriers of electricity are now known to be electrons and positively charged atoms, they continue to be designated by the old and convenient term of **thermions**. The electric current from a heated body is called a **thermionic current**. The temperature to which a body must be raised in order to produce an appreciable thermionic current depends upon the nature of the body and upon the nature and pressure of the surrounding gas. In a vacuum, this temperature is about  $1000^{\circ}$  for platinum, whereas for sodium a considerable thermionic current is produced at even  $300^{\circ}$ . The thermionic emission from heated oxides is frequently more than 1000-fold greater than that from platinum at the same temperature. The thermionic current increases rapidly with rise in temperature. For pure platinum in a good vacuum the current is nearly 100 times as great at  $1500^{\circ}$  as at  $1357^{\circ}$ ; the current being of the order of  $10^{-8}$  ampere per square centimeter at the lower temperature.

The emission of electrons from a heated body is often increased by the presence of small quantities of different gases, notably of hydrogen. For instance, in an atmosphere of hydrogen at a pressure of 0.0006 mm of mercury, the thermionic current from platinum at  $1350^{\circ}$  is 2500 times greater than that from the metal in a vacuum. In the presence of the same gas, thermionic currents as high as 1000 amperes per square centimeter have been obtained from heated lime.

An important application of the thermionic discharge has been made in the audion or radiotube, which is employed to amplify the currents set up in wireless receivers. The principle upon which this amplification depends has been discussed briefly in an earlier chapter (see p. 81). The introduction of the thermionic tube has made possible many accurate measurements in the field of chemistry as well as in physics.

(b) *The Conductance of Flames.* For more than a century, it has been known that flames and the gases coming from them are capable of conducting electricity. For instance, if two pieces of metal are placed in a wide Bunsen flame and one of them is raised to a moderately high potential, a feeble current will flow between them owing to the presence of ions in the flame gases. The strength of the current, which increases

with the potential and which shows no indication of attaining a saturation value, is practically independent of the distance between the electrodes as long as they remain in the flame. The current also increases with the temperature of the electrodes. The electric field is very intense in the neighborhood of the negative electrode and very weak, but uniform, through the remainder of the flame, except for a slight increase in strength near the positive electrode. Accordingly, the greater part of the resistance of the flame to the passage of the current is near the negative electrode.

(c) *The Conductance of Salt Vapors.* The current which flows between electrodes placed in a Bunsen flame is increased by the presence of salts (especially of the alkali metals) in the flame. The magnitude of the increase depends upon the nature of the metal of the salt, but is independent of the negative constituent. Wilson<sup>1</sup> concluded that the increase in conductance is due to a conversion of the salt into metallic vapor, which dissociates partially into metallic ions and electrons. Moreau<sup>2</sup> showed that with strong electric fields ionization also results from collision of electrons with vaporized alkali metal atoms. The increase in conductance is appreciable only when the salt is introduced near the negative electrode, since, as has been pointed out, it is in this region that practically the whole fall of potential takes place. By coating the negative electrode with a salt of an appropriate metal, the current may be increased as much as 1000 times for the same potential difference between the electrodes. If one of the electrodes is coated with a salt and an alternating electromotive force applied, a large current will flow through the flame when this electrode is negative and a small one when it is positive, thus practically permitting the current to flow in a single direction. An arrangement such as this might be employed as a rectifier.

The current  $I$  which flows between two electrodes not too widely separated in a flame is given approximately by the expression

$$E = A^2 \alpha I^2 \quad (4)$$

where  $E$  is the potential difference between the electrodes,  $c$  is the concentration of the salt vapor in the flame, and  $A$  and  $\alpha$  are constants. Therefore, the current varies directly as  $\sqrt{cE}$ . According to equation 4, the current should be zero when  $c$  is zero; but, as pointed out previously, a small current flows when no salt is present, owing to the ions in the flame gases.

<sup>1</sup> *Trans. Am. Electrochem. Soc.*, **44**, 127 (1923).

<sup>2</sup> *Ann. chim. phys.*, **24**, 289 (1911).

The value of the first constant in equation 4 is the same for all salts of the same alkali metal, but it decreases as the atomic weight of the metal increases; that of the second constant is nearly the same for all alkali metal salts, indicating that all alkali metals give ions having the same mobility. Wilson<sup>1</sup> found that owing to a potential gradient of 1 volt per centimeter in a Bunsen flame the velocity of the negative ions was probably about 7000 centimeters per second, and that of the positive ions only 1 or 2 centimeters per second. The high velocity of the negative ions indicates that they must be electrons at least during part of their existence. If the flame is not very hot or if the electric field is weak, the electrons may be combined with neutral atoms for a part of the time.

The percentage of alkali metal vapor which ionizes in a Bunsen flame increases rapidly with the atomic weight of the metal. When the concentration of the salt is small it has the following values:<sup>2</sup> caesium, 91; rubidium, 69; potassium, 58; sodium, 1.6; and lithium, 0.2 per cent. The relative concentrations of alkali metals giving the same conductances in a Bunsen flame, under the same conditions, are:<sup>3</sup> caesium, 1.0; rubidium, 4.5; potassium, 7.3; sodium, 626; and lithium, 4300.

In the flaming arcs, calcium fluoride and cerium chloride are used. The carbon electrodes are cored, the core consisting of a mixture of carbon and the salts. The electric magnetite arc depends for light production solely on the luminescence of the conducting vapors produced at the cathode. The anode consists of a thin iron tube, closely packed with a uniform mixture of magnetite, oxide of titanium, and oxide of chromium. The cathode is a block of copper of large heat-radiating capacity.<sup>4</sup>

**Positive Rays and Positive-Ray Analysis.** As we have seen, cathode rays consist of rapidly moving electrons. These electrons on collision with the molecules of the gas in a discharge tube remove one or more outer electrons, thus giving rise to positively charged particles which are immediately repelled by the anode and move with a high velocity towards the cathode. The presence of these **positive rays** in a discharge tube can be demonstrated by making a hole in the cathode normal to its surface, whereupon they can be observed streaming through and producing a phosphorescence in the gas behind this electrode. The color of this phosphorescence is quite different from that produced by cathode rays.

<sup>1</sup> *Trans. Am. Electrochem. Soc.*, **44**, 127 (1923).

<sup>2</sup> Wilson, *loc. cit.*

<sup>3</sup> Wilson, *loc. cit.*

<sup>4</sup> Cf. Pender, *Handbook*, p. 904, 1922; Compton, *Phys. Rev.*, **21**, 266 (1923); Moore, "Chemistry of Flaming Arc Carbons," *Trans. Am. Electrochem. Soc.*, **27**, 435 (1915); Mott, *ibid.*, **31**, 365 (1917); Darrah, *ibid.*, **29**, 613 (1916); G. M. J. MacKay and Ferguson, *J. Franklin Inst.*, **181**, 209 (1916).

J. J. Thomson developed an ingenious method for determining the individual masses of the particles constituting positive rays. This method was improved by Aston,<sup>1</sup> who has perfected an apparatus for positive-ray analysis which he calls a **mass spectrograph**.

The mass spectrograph is shown diagrammatically in Fig. 87. In this instrument the positive rays, after coming through perforations in the cathode, pass through two narrow slits,  $S_1$  and  $S_2$ , which permit a thin band of the rays to pass through the electric field between the charged plates,  $P_1$  and  $P_2$ , where it is spread out into an electric spectrum. On leaving the electric field, the rays may be considered as radiating from

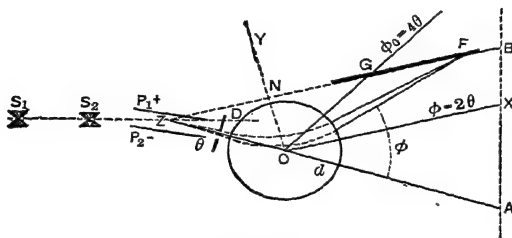


FIG. 87.

a virtual source,  $Z$ , midway through the field on the line  $S_1S_2$ . A portion of the rays, deflected through an angle  $\theta$ , passes first through a diaphragm  $D$ , and then through the magnetic field of the powerful electromagnet,  $O$ . This field is arranged so as to produce a deflection of the rays through an angle,  $\phi$ , which is more than twice as great as  $\theta$ , and in a direction opposite to that produced by the electric field. In this manner, all particles having the same ratio of charge to mass, though differing in velocity, are brought to a focus at the same point,  $F$ , on the photographic plate  $GF$ . Thus, each kind of charged particle will produce its own image at a different and definite focus. The series of images obtained in this way is called a **mass spectrum**. By comparing the positions of the images produced by particles of unknown mass with that of the image produced by a particle whose mass is known, it is possible to determine the mass of the unknown particles. If the distances of two images from a chosen point of reference are  $l_1$  and  $l_2$  and the corresponding masses are  $m_1$  and  $m_2$ , the value of the ratio,  $m_1/m_2$ , will be the same in every experiment for given values of  $l_1$  and  $l_2$ . In this way atomic weights can be determined with an accuracy of about 0.1 per cent.

Taking the mass of the oxygen atom as 16.00, the mass of some elements as determined by the mass spectrograph is a whole number.

<sup>1</sup> *Phil. Mag.*, **38**, 709 (1919).

Where masses are found which differ from whole numbers, it has been found that the elements (so-called) consist of a mixture of **isotopes**, i.e., elements having identical chemical properties but different atomic weights. Table CXXXI contains a list of elements and their isotopes.

TABLE CXXXI

## ATOMIC WEIGHTS OF ELEMENTS AND ISOTOPES

* Element	Atomic Weight	No. of Isotopes	Atomic Weight of Isotopes
H	1.008	1	1.008, 2.0136
He	4.00	1	4
Li	6.94	2	7, 6
B	10.9	2	11, 10
Mg	24.36	3	24, 25, 26
Si	28.3	2	28, 29, 30
Cl	35.46	2	35, 37
A	39.9	2	40, 36
K	39.10	2	39, 41
Ca	40.07	2	40, 44
Zn	65.37	4	64, 66, 68, 70, 65, 67, 69
Br	79.92	2	79, 81
Kr	82.92	6	78, 80, 82, 83, 84, 86
Rb	85.45	2	85, 87
Xe	130.2	7	128, 129, 130, 131, 132, 134, 136
Hg	200.6	6	197, 198, 199, 200, 202, 204

The mass spectrum of neon is reproduced in Fig. 88. The two lines produced by this element correspond to the atomic weights 20 and 22, while the lines at 16, 24, 26, and 28 correspond to oxygen, carbon ( $C_2$ ), acetylene, and ethylene or carbon monoxide, respectively. Aston concludes from this result that neon consists of two isotopes differing in

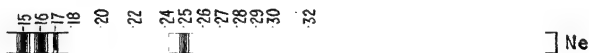


FIG. 88.

atomic weight by two units, rather than of one species of atoms having an atomic weight of 20.2, the commonly accepted atomic weight of neon.

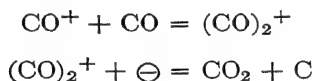
**Electrochemical Action in Gases.** During electrolysis electrochemical action takes place solely at the electrodes, "and separation of the products may be regarded as a necessary consequence of the liquid-solid boundary existing there."<sup>1</sup> Chemical action accompanying electrical

<sup>1</sup> Lind, *Trans. Am. Electrochem. Soc.*, **44**, 63 (1923).

discharge through gases is a much more complicated phenomenon than that which takes place during electrolysis. As Lind points out, ionization and the reverse discharge by ionic recombination take place not at the electrodes, but mainly in the interior of the gas; and "such chemical action as may result has no direct relation to the current flowing and is usually greatly in excess of it, but does have a relation to the ionization."

The study of chemical action accompanying electrical discharge through gases has been carried out at very low gas pressures, where considerable progress has been made, and at normal or even higher pressures, where development has been slow and somewhat empirical, owing to a lack of knowledge as to the nature of the ions and the extent of ionization at high gas pressures. The importance of investigation of chemical action in ionized gases at high pressures has been emphasized by Lind,<sup>1</sup> who pointed out that "if we are to have an electrochemistry of gases which shall occupy an important position in preparative chemistry, comparable to that of electrolytic chemistry, it will be in the region of relatively high, not of low, gas pressure discharge."

During an electrical discharge through a gas, but a small fraction of the molecules is ionized. These molecules are in a chemically active condition. For example, positive-ray analysis shows the temporary existence in electrical discharge tubes of *diatomic* molecules of the inert gases, and of *compounds* of these gases with hydrogen. Evidence has been obtained which indicates not only that gaseous ions are chemically active, but also that they constitute the *intermediate activated products* of reaction. Thus, in the formation of carbon dioxide in ionized carbon monoxide, two molecules of carbon monoxide are decomposed for each molecule of the gas ionized.<sup>2</sup> The reaction, apparently, takes place in accordance with the equations



From this and other electronic evidence, Lind<sup>3</sup> put forward the following general laws:

1. Free electrons will play a primary role in promoting chemical reaction of gases only when a gas is present capable of forming a negative ion by attaching the free electrons. A secondary role is always played by electrons in restoring final electrical neutrality.
2. Gas ions tend to form charged complexes by attaching themselves

<sup>1</sup> *Trans. Am. Electrochem. Soc.*, **44**, 63 (1923).

<sup>2</sup> Cf. Lind and Bardwell, *J. Am. Chem. Soc.*, **45**, 2585 (1923).

<sup>3</sup> *Trans. Am. Electrochem. Soc.*, **44**, 63 (1923).

to electrically neutral molecules. *These complexes are the intermediate compounds of chemical reactions.*

3. Activated molecules or atoms do not interact among themselves, but they react with the unactivated molecules.

4. Ineffective encounters may destroy the activity of one of the components by leading to the reverse reaction.

Many investigators believe it more probable that chemical reactions in an electric discharge are the result of the production of atoms and radicals, rather than ion clusters, as intermediaries.<sup>1</sup> According to Harteck,<sup>2</sup> hydrogen atoms produced in a glow discharge tend to remove hydrogen from organic molecules with the formation of radicals; e.g.,  $C_2H_6 + H = C_2H_5 + H_2$ . Reactions carried out with slow electrons have shown that products can be formed below the ionizing potential of the reacting gases. For example, it has been found<sup>3</sup> that ammonia is decomposed by electrons of  $9 \pm 1.4$  electron volts, even though its ionizing potential is 11.2 e.v.

Although the number of electrochemical gas reactions runs into the thousands, it is possible to refer to but a very few here.

In the presence of an electric glow discharge, helium and mercury vapor combine to form a compound the simplest formula for which is  $HgHe_{10}$ .<sup>4</sup> When mercury is subjected to intense electronic bombardment at low pressure in contact with a heated tungsten filament, it is probable that a stable compound is formed. Helium has been found to disappear from mixtures with the vapor of sulphur, phosphorus, and iodine when subjected to electronic bombardment in the vicinity of surfaces cooled with liquid air, solid products being produced.<sup>5</sup> Various chemical actions are brought about by the influence of  $\alpha$  particles from radon.<sup>6</sup> For example, saturated hydrocarbons condense, methane and carbon dioxide combining to form a waxlike solid. Similar actions are effected by the  $\beta$  and  $\gamma$  rays of radium.<sup>7</sup> The formation of acetylene from mixtures of methane and hydrogen, in an alternating-current discharge tube, increases with the frequency,<sup>8</sup> the best yield (117.5 liters per

<sup>1</sup> Cf. Eyring *et al.*, *J. Chem. Phys.*, **4**, 570 (1936); Emeléus and Lunt, *Trans. Faraday Soc.*, **32**, 1504 (1936); Lunt and Swindell, *ibid.*, **36**, 1072 (1940); Steacie and Brown, *J. Chem. Phys.*, **8**, 734 (1940).

<sup>2</sup> *Rundschau tech. Arb.*, **17**, 2 (1937).

<sup>3</sup> Schwab, *Z. anorg. allgem. Chem.*, **236**, 296 (1938).

<sup>4</sup> Manley, *Nature*, **114**, 86 (1924).

<sup>5</sup> Booner, *Proc. Roy. Soc.*, **A109**, 198 (1925).

<sup>6</sup> Lind and Bardwell, *J. Am. Chem. Soc.*, **46**, 2003 (1924); **47**, 2675 (1925); **48**, 2335 (1926).

<sup>7</sup> Errera and Henri, *J. phys. radium*, [vi], **7**, 225 (1926).

<sup>8</sup> Briner and co-workers, *Helv. Chim. Acta*, **21**, 1570 (1938).



kilowatt-hour) being obtained at a pressure of 730 mm, a frequency of  $10^7$  cycles, and 32–36 liters of hydrogen and 4–8 liters of methane per hour. The gas formed by passing an interrupted discharge through anthracene oil has been found to contain 22–30 per cent of acetylene.<sup>1</sup> The passage of a high-frequency electric discharge through either acetylene or mixtures of this gas with hydrogen or ethylene results in the formation of butadiene.<sup>2</sup> This diene is also formed from ethylene in the high-frequency corona discharge.<sup>3</sup> When a high-frequency arc is passed through illuminating gas which has been diluted with 40 per cent nitrogen, 27.2 grams of hydrogen cyanide and 3 grams of ammonia per kilowatt-hour are obtained.<sup>4</sup> Monochloroacetic acid has been produced by applying a silent discharge to a mixture of acetic acid and red phosphorus through which chlorine gas is passed.<sup>5</sup>

Although it had been stated frequently in the literature that Faraday's law is applicable to gas reactions in the silent discharge, from an extensive and critical review of such reactions Warburg concluded<sup>6</sup> that, in general, the amount of chemical action is *not* proportional to the quantity of current used. For example, Pohl found that the quantity of electricity required to decompose one mole of ammonia in the silent discharge varies from 1950 to 6500 coulombs, depending on conditions.<sup>7</sup>

**The Coolidge Cathode-Ray Tube.** A source of intense cathode rays (electrons), which proved valuable in the study of electrochemical action in gases, was developed by W. D. Coolidge.<sup>8</sup> This is a cathode-ray tube for the production of high-voltage cathode rays outside of the generating tube. A diagram of one model of this tube, used for potentials up to 250,000 volts, is shown in Fig. 89.

"The cathode consists of a flat spiral of tungsten wire placed in a hemispherical focusing cup, *c*.

"The anode proper, *a*, is at the same time the window, and consists of a sheet of nickel foil 0.0127 millimeter thick and 7.5 centimeters in diameter, supported against the pressure of the atmosphere by a honey-comb structure of molybdenum, *b*. The edge of the window is soldered to the invar ring, *r*, and this in turn is sealed directly to the end of the glass anode arm, at *s*.

"A long copper tube, *k*, electrically connected to the window, serves as

<sup>1</sup> Kushnerev and Shekhter, *J. Phys. Chem. U.S.S.R.*, **13**, 259 (1939).

<sup>2</sup> Balandin, Eidus, and Terent'eva, *Compt. rend. acad. sci. U.R.S.S.*, **27**, 343 (1940).

<sup>3</sup> Eidus, *Bull. acad. sci. U.R.S.S.*, **1938**, 737.

<sup>4</sup> Briner and Hoefer, *Helv. Chim. Acta*, **24**, 1006 (1941).

<sup>5</sup> Isomura, *Bull. Chem. Soc. Japan*, **14**, 258 (1939).

<sup>6</sup> *Z. tech. Physik*, **4**, 450 (1923); **5**, 165 (1924); **6**, 625 (1925).

<sup>7</sup> *Ann. Physik*, **21**, 879 (1906).

<sup>8</sup> *Science*, **62**, 441 (1925); *J. Franklin Inst.*, **202**, 693 (1926).

an electrostatic shield to protect the glass of the anode arm from puncturing.

"This shield is very essential to high-voltage operation as, without it, full cathode potential may build up on the inside of the glass anode arm, even in the immediate neighborhood of the anode, resulting in a potential gradient which will cause destructive disruptive discharges through the glass.

"As a result of the presence of the shield, very few electrons can get to the glass walls of the tube. For most of the electrons constituting the

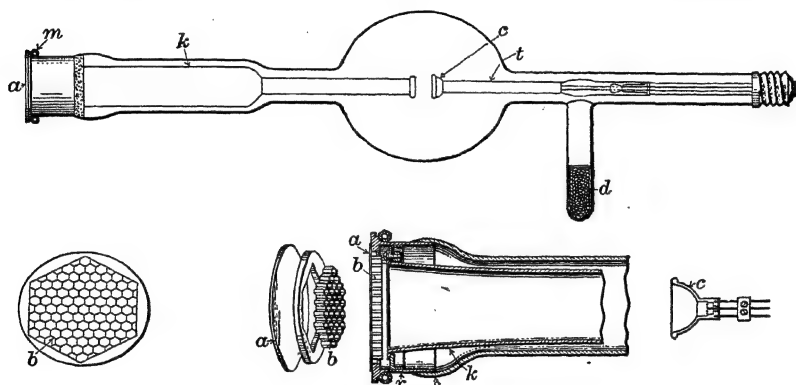


Diagram of cathode-ray tube

FIG. 89.

cathode-ray stream go right through the window, and, of those reflected from the window and the window support, nearly all will go to the shield and only a relatively very small number can emerge from the end of the shield facing the cathode against the hostile field of the latter.

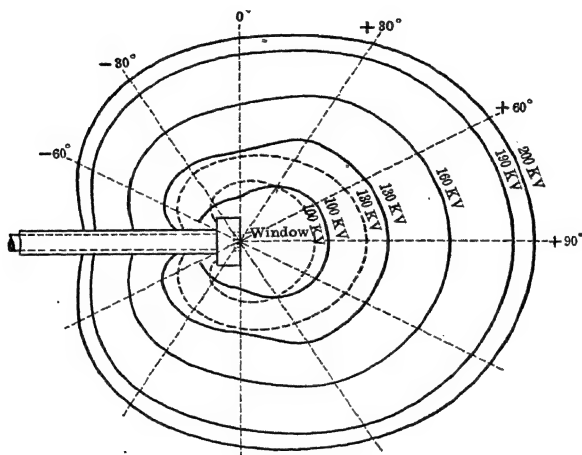
"The bulb is 20 centimeters in diameter and the overall length of the tube is 89 centimeters."

The variation of the range of the cathode rays outside of the tube with the operating voltage is shown diagrammatically in Fig. 90. It will be observed that, when generated with a potential of 200 kilovolts, the cathode rays have a range of 36 centimeters in air, and that the rays bend round until they extend more than half their range backwards to the tube.

By means of the Coolidge tube it is possible to pass electrons at a high voltage into a reaction mixture in sufficient quantity to yield enough product for analysis. Busse and Daniels<sup>1</sup> utilized this source to study

<sup>1</sup> *J. Am. Chem. Soc.*, **50**, 3271 (1928).

the effect of cathode rays on oxygen, nitric oxide, air, and carbon dioxide. They found that the number of molecules decomposed or produced per electron crossing the cathode-ray tube was: nitric oxide decomposition, 230; ozone formation from oxygen, 100; ozone formation from air, 44; nitric oxide formation from air, 14; carbon dioxide decomposition, 3. The decomposition of a number of paraffin hydrocarbons was brought about <sup>1</sup>



Scale in Centimeters

FIG. 90.

by high-speed electrons (125,000 volts) obtained through the window of a Slack <sup>2</sup> high-speed cathode-ray tube. The nature of the decomposition is similar to that effected by  $\alpha$  particles. Hydrogen is one of the decomposition products, about 1000 molecules being formed per electron entering the reaction vessel.

**Chemical Action in the High-Voltage Discharge through Air.** The chemical action of all electrical discharges through air consists, fundamentally, of the formation of two endothermic compounds—ozone and nitric oxide. Although the proportions of the substances in the equilibrium gas mixture increase with rise in temperature, the rates at which the compounds decompose also increase rapidly with temperature. Since immediate decomposition of ozone takes place at 200° and of nitric oxide

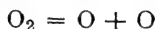
<sup>1</sup> Lind, Marks, and Glocker, *Trans. Electrochem. Soc.*, **59**, 157 (1931).

<sup>2</sup> Slack, *J. Am. Optical Soc.*, **18**, 123 (1929).

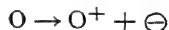
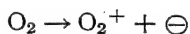
at 1200°, the concentrations of these gases which result in an electric discharge depend upon the temperature and upon the speed with which they are removed from the region of high temperature. Obviously, only nitric oxide results in the flaming arc and in the spark discharge. In the brush discharge both nitric oxide and ozone are produced. The dark discharge, which is a comparatively cold discharge, is the most favorable type for the formation of ozone, and the least favorable for the production of nitric oxide.

According to Rideal,<sup>1</sup> the following steps occur in the formation of ozone in the electrical discharge:

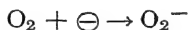
- (a) A splitting of the oxygen molecule into two neutral atoms



- (b) Ionization of the oxygen molecule or atom by collision with electrons



- (c) Ionization of the molecule or atom by collision and an adherence of an electron



Oppositely charged ions may then unite to form an ozone molecule <sup>2</sup>



The molecules which acquire a charge in an electric discharge, and the free electrons, move in the electric field with a high velocity. Since this high velocity is equivalent to a high temperature, the classical controversy whether the formation of nitric oxide in an arc is an electrical phenomenon or a thermal process becomes superfluous. As the distribution of the velocities of the molecules and ions in an electric field does not follow Maxwell's distribution law, it is not possible to ascribe a definite temperature to the discharge and, accordingly, "thermodynamic calculations based on a definite temperature of an arc or an electrical discharge are unsound. The gas immediately surrounding

<sup>1</sup> *Ozone*, p. 107, 1920.

<sup>2</sup> Otto and Bennett (*J. Chem. Phys.*, 8, 899 [1940]) attribute the formation of ozone in the silent discharge to collisions intermediate between ionizing and attaching energies, while Joshi (*Current Sci.*, 8, 548 [1940]) finds that a threshold potential is necessary for the reaction.

such a region does have a 'real' temperature, and this temperature determines the thermodynamic equilibrium of the gases which leave the arc. It is evident that the concentration of endothermic compounds in the electrical field may be much greater, but it cannot be calculated quantitatively because a definite temperature cannot be ascribed to it. Furthermore, it is of little importance anyway, for the products cannot be removed without going through this region of lower kinetic energy, where a real equilibrium with a lower concentration of endothermic compounds is established. For calculations of equilibrium then the temperature should be that of the region immediately surrounding the electrical discharge but outside of the electrical field."<sup>1</sup> It can be said, therefore, that an electrical equilibrium exists which gives a greater concentration of nitric oxide and ozone than the thermal equilibrium.<sup>2</sup>

The technical production of nitric oxide and ozone in the electrical discharge is discussed by Koehler in Vol. II.

In addition to the formation of ozone and nitric oxide in the electrical discharge through air, several secondary reactions may take place to an extent depending upon the nature of the discharge. At temperatures below 600° nitric oxide unites with the oxygen of the air to form nitrogen peroxide, which below 120° polymerizes to nitrogen tetroxide. Nitrogen trioxide is also formed by the union of nitric oxide and nitrogen peroxide. At moderately low temperatures nitrogen pentoxide is formed by the oxidation of the other oxides of nitrogen by ozone. The formation of gaseous ions in the oxidation of nitric oxide has been discussed by Brewer and Daniels.<sup>3</sup> Lind and Glocker<sup>4</sup> have condensed ethane, propane, and butane by a silent discharge at 12,000 volts, the condensations being similar to those produced by  $\alpha$  rays.

**The Disappearance of Gas in the Electric Discharge.** Investigation of chemical action accompanying electrical discharge through gases at very low pressures led to a study of the disappearance or "clean up" of the gases in discharge tubes. The disappearance of the gas is due to the *electrical discharge* and not primarily to any *direct chemical action*, since not a trace of clean up takes place unless the potential applied to the electrodes is sufficient to ionize the gas, and that, in general, the rate of disappearance of the gas increases with ionization.<sup>5</sup> The clean up is more rapid and complete if such elements as phosphorus, sulphur, iodine,

<sup>1</sup> Daniels, Keene, and Manning, *Trans. Am. Electrochem. Soc.*, **44**, 247 (1923).

<sup>2</sup> Holweh and Koenig, *Z. Elektrochem.*, **16**, 803 (1910).

<sup>3</sup> *Trans. Am. Electrochem. Soc.*, **44**, 257 (1923).

<sup>4</sup> *J. Am. Chem. Soc.*, **52**, 4450 (1930).

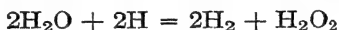
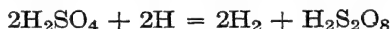
<sup>5</sup> Research Staff of the General Electric Company, Ltd. (England), *Phil. Mag.*, **40**, 585 (1920).

arsenic, sodium, and potassium are deposited on the cathode of the discharge tube.<sup>1</sup> With hydrogen and nitrogen, the rate of disappearance of the gas is greatest with the first three of these elements, and the final pressure attained is a minimum with phosphorus and sulphur.<sup>2</sup>

A study of clean-up reactions was made in the Research Laboratories of the General Electric Company,<sup>3</sup> this process being involved in the manufacture of all electric incandescent vacuum lamps, audions, X-ray tubes, Dewar flasks, etc.

Atomic hydrogen,<sup>4</sup> oxygen,<sup>5</sup> and chlorine,<sup>6</sup> which are readily prepared by electrical discharges through the gases at low pressure, are opening up new fields in chemistry, especially in the preparation of new inorganic compounds.<sup>7</sup>

**Glow Discharge Electrolysis.** In this type of electrolysis,<sup>8</sup> which has been extensively studied by Klemenc and his co-workers,<sup>9</sup> either one or both of the electrodes are located in the gas phase over the solution to be electrolyzed. With the cathode in the vapor, potassium chlorate, potassium bromate, and chromic acid have been reduced to an extent of about 90 per cent; and both chloric and perchloric acids have been reduced more readily than in ordinary electrolysis, the current yield being much greater than that which corresponds to Faraday's law. Accordingly, it has been concluded that in glow discharge electrolysis "active" uncharged particles participate in the electrochemical process. Thus, the formation of persulphuric acid and hydrogen peroxide is attributed to hydrogen atoms produced by the decomposition of water vapor:



<sup>1</sup> Cf. Whitney, *Trans. Am. Inst. Elec. Engrs.*, **31**, 921 (1921); Newman, *Trans. Am. Electrochem. Soc.*, **44**, 77 (1923).

<sup>2</sup> Newman, *loc. cit.*

<sup>3</sup> A complete survey of the earlier work on the clean up of gases was made by Dushman, *Gen. Elec. Rev.*, **24**, 436, 669 (1921).

<sup>4</sup> Wood, *Phil. Mag.*, **42**, 729 (1921); **44**, 538 (1922); Bonhoeffer, *Z. physik. Chem.*, **113**, 199 (1924); **119**, 385 (1926).

<sup>5</sup> Wrede, *Z. Physik*, **54**, 53 (1929); Harteck and Kopsch, *Z. physik. Chem.*, **12B**, 327 (1931).

<sup>6</sup> Schwab and Friess, *Naturwiss.*, **21**, 222 (1933); Rodebush and Klingelhoefer, *J. Am. Chem. Soc.*, **55**, 130 (1933).

<sup>7</sup> Cf. Bowen, *Chem. Soc. Ann. Repts.*, **1933**, 46.

<sup>8</sup> Cf. Haber and Klemenc, *Z. Elektrochem.*, **20**, 285 (1914).

<sup>9</sup> *Z. physik. Chem.*, **A130**, 378 (1927); **A154**, 385 (1931); *Z. Elektrochem.*, **37**, 742 (1931); *Z. physik. Chem.*, **A166**, 343 (1933); **B27**, 359 (1934); **B40**, 252 (1938); **A183**, 297 (1939); *Z. anorg. allgem. Chem.*, **240**, 167 (1939); cf. also Jolibois, *Bull. soc. chim.*, **5**, 1429 (1939); de Beco, *Compt. rend.*, **208**, 797 (1939).

According to Klemenc, the observed effects in glow discharge electrolysis are separable into apolar and polar. Chemical changes brought about by the polar effects are claimed to conform with Faraday's law. Those which are effected by the apolar process, and which are operative both in the gas space and in the liquid, often differ from those brought about by ordinary electrolysis. The sum of the polar and apolar effects is in excess of the Faraday equivalent.

**Summary.** In recent years there has been a great deal of activity in the study of the electrochemistry of gases, a field in which it is relatively simple to control conditions such as energy input and temperature. Many investigations on the polymerization, synthesis, and cracking of hydrocarbons in both the silent discharge and the spark discharge have been carried out in the United States, Russia, and Japan. However, even though it has been found that liquid, petroleum-like products may be formed from gaseous hydrocarbons in discharge tubes, as yet no technical application has been made. Indeed, of all the thousands of reactions studied, the production of ozone is the only one that is of practical importance at the present time.

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